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ANALYTICAL METHODS OF MANGANESE ORES II.

Contribution to the determination of zinc and titanium in manganese ores

by

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INTRODUCTION

In one of his earlier papers [GRASSELLY, 1961] dealing with rapid methods of analysis of manganese ores, the author proposed new method for the separation of the Fe—Al—Mn—Ca—Mg content, by ion exchange technique using the corresponding complexometric method for the determination of the single components.

Extending the rapid methods on further components, the present paper is dealing on the one hand, with the possible errors due to the presence of Ti and with the problem of the most purposeful determination of Ti in the analytical process developed earlier, on the other hand, with method of analysis of manganese oxides for zinc.

EXPERIMENTAL

According to the analytical process described in the paper reffered, the separation of Fe—Al—Mn—Ca—Mg is performed by using a cation exchanger Wofatit KPS—200 [Cl⁻]. To the aliquot parts of 50 ml — taken from 500 ml of stock solution prepared after the dissolution of 1 g of manganese ore — 0,05 M EDTA solution is added in excess about of 50 p. c. compared to the amount necessary for complexing the expected Fe+Al content of the aliquot. The solution is then adjusted by acetate buffer to pH 3,5; after boiling it is cooled down, let finally washed with 150 ml of water. Fe+Al will be present in the effluent, while the other components remain in the column, from where at proper pH value, they can be eluted and determined separately, using a given excess of 0,05 M EDTA. The pH value of the effluent is adjusted to 5,6 by means of hexamethylenetetramine, and the excess of 0,05 M EDTA is titrated back by 0,05 M solution of zinc acetate against xylenolorange indicator. Thus, we obtain the amount of 0,05 M EDTA equivalent to that of Fe+Al present. On the other hand, iron has already been titrated at pH 2—3 in a similar volume of stock solution, so that the quantity of Al can be given by the difference

of these two measurements. Here we are faced with the question as to how the above-outlined working process should be modified for additional two components, Zn and Ti, and how the determination of these two components could be fit in the most suitable way in the given set of analyses.

1. Determination of zinc

The various manganese oxides, such as chalcophanite [$ZnMn_3O_7 \cdot 3H_2O$], franklinite [$(Zn,Mn,Fe)(Fe,Mn)_2O_4$], woodruffite [$(Zn,Mn)_2 \cdot Mn_5O_{12} \cdot 4H_2O$], hetaerolite or hydrotaerolite [$ZnMn_2 \cdot (O,OH)_4$] or Zn-bearing todorokite, contain more or less zinc, too. In addition, the determination of zinc may also be of interest for the study of various ferrites.

If a solution contains, along with Fe—Al—Mn—Ca—Mg, some Zn too, then under the circumstances of the above method, zinc will get in the effluent solution, together with iron and aluminum. For instance, under the given circumstances 32,06 mg of Zn was introduced into the column and 31,95 mg of Zn was found in the effluent. Error equals 0,11 mg. Consequently, if the effluent contains some Zn, the available method of determination of Fe and/or Al can no longer be applied unreservedly, because Zn must either be masked or previously removed.

This latter seems to be the more suitable approach for the simple reason that the expected zinc content is as a rule smaller than that of Fe(Al) or especially that of Mn (unless explicitely Zn-bearing manganese ores, such as those mentioned previously, but manganese ores having Zn-bearing manganese oxide components too, are under consideration), so that the ion exchange technique used for the separation of zinc may serve as enrichment technique as well.

a) Possibilities of separating zinc from other cations by using anion exchangers

In analysing ferrites DONALD H. WILKINS [1959] applies a strongly basic anion exchanger resin for the separation of zinc, cobalt, nickel, and iron. The Ni content of the solution (9 N for hydrochloric acid) passes through the anion exchanger column and can be washed out quantitatively with 9 N hydrochloric acid, whereas the chlorocomplexes of Co, Fe, and Zn will remain in the resin bed, from where they can be eluted, first the Co by 4 N hydrochloric acid, then the Fe by 0,5 N hydrochloric acid. Finally, Zn is eluted by 3 N nitric acid. The eluates are evaporated in order to remove the excess of acid. Thereafter, they are taken up by water and after adding of EDTA solution in excess the pH is adjusted to 4,8. The excess of EDTA is then titrated back by standard $CuSO_4$ solution using PAN indicator. After the elution of zinc the column is rinsed by water, then regenerated by washing it with hydrochloric acid.

Similar experiments were run by D. JENTZSCH and I. FROTSCHER [1954]. They used anion exchanger Wofatit L—150 for the separation of cations. The method was similarly based upon the different adsorption properties of the chloro-complexes. The separation of the individual components was performed by means of elution on the column, using solutions with decreasing hydrochloric acid concentrations. The Ni introduced in 10 N hydrochloric acid, passes through the column, whereas Co remains in the column, from where it can be eluted by 6,5 N hydrochloric acid.

In his book PŘIBIL [1961] refers to the paper of A. M. AMIN and N. I. FARAH [1955]. According to this paper the zinc is separated also by anion exchanger in form of chloro-complexes from the other components. These authors propose to use anion exchanger Amberlite IRA—400 treated previously with 2 N hydrochloric acid. Again, the solution is introduced into the top of the column in 2 N solution of hydrochloric acid. The zinc is retained in the bed from where it can be eluted by water and 0,025 N nitric acid.

b) *Separation of zinc from iron, aluminum, manganese, calcium, and magnesium in manganese ores*

As shown in the above discussion, under proper circumstances Zn can be separated in 2 N solution of hydrochloric acid already and one need not use 10 N or 9 N solutions of hydrochloric acid. This approach is so much the more advantageous, as on the one hand, after the weighed sample of manganese ore has been dissolved, zinc can be removed in this way by anion exchanger from each aliquot part of stock solution before the separation of Fe+Al+ +Mn+Ca+Mg. By evaporation of the effluent the excess of acid can be removed and the solution can be introduced into the cation exchanger in order to separate the other cations. On the other hand, the zinc eluted from the anion exchanger, can be quantitatively determined. However, if an extremely small quantity of zinc is only expected, it is useful to introduce all the solution obtained by dissolving the manganese ore sample into the anion exchanger, so that the whole zinc content of the sample will be enriched in the bed.

Now the following questions will only have to be answered: Under the given conditions (Amberlite IRA—400; grain size 0,2 mm ∅; inner diameter of resin column 10 mm; height of resin column 100 mm) and in presence of the cations taken into consideration, in solutions of hydrochloric acid of what normality does zinc remain quantitatively on the column? Under which circumstances can it be eluted? Is the separation of the other cations — such as Fe, Al, Mn, Ca, and Mg — from zinc perfect?

Sorption step

Using 2 N and (in another run) 0,5 N solutions of hydrochloric acid, aliquot parts of solution of known zinc content were introduced into the anion exchanger which, in turn, had been washed out previously with 2 N and 0,5 N hydrochloric acid, respectively. After the zinc-bearing solution passed through the resin column, the latter was washed with 5×20 ml of 2 N or (in the other run) 0,5 N hydrochloric acid. In the effluent solution zinc could not be determined, it remained quantitatively in the bed either 2 N or 0,5 N hydrochloric acid was used.

Elution step

We first attempted to perform the elution of zinc with water and 0,025 nitric acid, as described in the paper of AMIN and FARAH, but under the given circumstances the zinc could not be completely eluted from the column even when washed for a long time.

We found, however, another, more successful approach. After washing with 2 N or 0,5 N hydrochloric acid, the collected effluent and wash liquid is put aside (any cations other than zinc will be present in these solutions), the resin bed is washed first with 10 ml of water, then with 20 ml of ammonium-ammonium chloride buffer solution diluted 1:1 (which is used in complexometric titration against indicator Eriochromblack T for adjusting pH to 10) and finally with 3×10 ml of water, too. The amount of zinc is determined in this collected solutions titrated by 0,05 M EDTA against Eriochromblack T indicator. Under these conditions, the elution is perfect. The

amounts of zinc found in the eluates correspond well to those determined in the aliquot parts of stock solution, as illustrated in Table 1.

TABLE 1.

Amount of Zn in mg		Amount of Zn in mg	
Added	Determined	Added	Determined
in 2 N hydrochloric acid		in 0,5 N hydrochloric acid	
6,70	6,67	12,28	16,28
9,97	9,94	32,56	32,59
16,41	16,38	48,84	48,74
		80,74	80,84

Thereafter the regeneration of the column can follow by 2 N and 0,5 N hydrochloric acid, respectively.

As mentioned previously, an additional question was, whether the other cations present under similar circumstances would get into the effluent solution, or not, whilst the zinc is retained quantitatively in the bed.

Therefore, known quantities of the single cations were added separately into the anion exchanger, using 2 N solution of hydrochloric acid in the first run and 0,5 N in the second one. After the effluent solution has dropped, the bed is washed with 5×20 ml of 2 N and 0,5 N hydrochloric acid, respectively, the solution is evaporated and the amount of the cations is determined complexometrically. The data obtained in this way are shown in Table 2.

It follows from the above that the occasional zinc content of manganese ores can be separated from the other cations and then determined, as follows:

1. 50 ml aliquots (if greater amount of zinc are expected) of the stock solution prepared by dissolving the manganese ore sample (as described in the introductory paper quoted above) are evaporated, the residue is taken up by 0,5 N hydrochloric acid and the solution is let pass through an anion exchanger Amberlite IRA—400 treated formerly with 0,5 N hydrochloric acid. Then the column is washed with 5×20 ml of 0,5 N hydrochloric acid. Zinc remains in the bed, the other components being present in the effluent.

2. The collected effluent and wash liquid is evaporated in order to remove the excess of acid. Afterwards, the residue is taken up by water, 0,05 M EDTA is added in excess of known amount, the pH is adjusted to 3,5, and the solution is introduced into a cation exchanger Wofatit KPS—200 for separating the other cations (see the first paper).

3. The anion exchanger is washed first with 10 ml of water, then with 20 ml of ammonium-ammonium chloride buffer diluted 1:1, finally with 3×10 ml of water. The amount of zinc in the eluate (diluted to 100 ml) is titrated by 0,05 M EDTA solution using Erioblack T as indicator.

(If a low zinc content is expected, it is advisable to prepare the stock solution a priori, in such a way that it should be 0,5 N for hydrochloric acid, and the whole stock solution is let pass through the anion exchanger. This time the zinc content of the whole weighed sample will concentrate in the anion exchanger. The anion exchange bed washed

TABLE 2.

Metals, in mg, added into the anion exchanger using and determined in the effluent solution				
0,5 N hydrochloric acid			2 N hydrochloric acid	
Added		Determined	Added	Determined
Fe	27,42	27,31 27,26 27,17 27,25	27,73	27,73 27,67 27,65 27,68
Al	13,29	13,35 13,34 13,33 13,34	13,17	13,22 13,22 13,22
Mn	27,11	27,08 27,08 27,08	27,39	27,25 27,30 27,36 27,30
Ca	10,20	10,18 10,16 10,20 10,18	20,10	20,08 20,12 20,14 20,11
Mg	6,08	6,14 6,15 6,13 6,14	12,18	12,18 12,19 12,18 12,18

with 0,5 N hydrochloric acid and the effluent is evaporated for removing of the bulk of the excess of acid. Thereafter, the residue is taken up and poured into a 500 ml measuring flask and filled up to the mark. From this solution aliquots of 50 ml are introduced into a cation exchanger Wofatit KPS—200.)

2. Determination of titanium

The influence of the presence of Ti on the set of analyses is worth of consideration, because minimal amounts of Ti may be present in manganese ores, too, due to the admixture of accessory mineral components, and also because the analytical process developed for manganese ores can certainly be applied, mutatis mutandis, to silicate analyses as well.

The presence of titanium raises the following questions:

a) Does titanium, during the separation outlined in section 1, pass into the effluent solution, together with iron and aluminum?

b) Is in the presence of titanium that precision method applicable to back titration of excess of EDTA which proved good in presence of iron+auminum?

c) Which method can be used most advantageously for the determination of titanium?

a) *The influence of the presence of titanium on the analytical process*

The solution used in the experiments contained merely titanium (1 ml= =0,195 mg TiO_2). In one set of analyses 0,05 M EDTA was given in known excess to aliquot parts of 10 and 25 ml, respectively, taken from the stock solution. Thereafter, the solution was adjusted to pH 5,6 by means of hexamethylenetetramine and the excess of EDTA was titrated back by 0,05 M zinc acetate solution against xylenolorange indicator, determining in this way the ml-s of EDTA equivalent with the titanium present. In the other set of analyses similarly 10 or 25 ml aliquots of Ti solution were taken and adjusted to pH 3,5 by acetate buffer. After the necessary excess of EDTA was added to the solution, it was let pass through a cation exchanger Wofatit KPS—200. As the excess of EDTA in the effluent solution was titrated back under the circumstances described above, the amount of titanium was similarly determined. The results are summarized in Table 3.

TABLE 3.

TiO_2 mg calculated	TiO_2 determined in aliquot parts of stock solution by back titration of the excess of EDTA mg	TiO_2 passed through ion exchanger, determined in effluent solution by titrating back the excess of EDTA mg
1,95 mg	1,87 mg 1,91 1,95 1,95 1,92 mg —0,03	1,96 mg 1,83 1,87 1,87 1,88 mg —0,07
4,87 mg	5,07 mg 5,03 4,95 4,95 5,00 mg +0,13	4,87 mg 4,87 5,03 4,97 4,93 mg +0,06

The above results show, on the one hand, that under the above circumstances the titanium content of the solution introduced into the cation exchanger Wofatit KPS—200 passes completely into the effluent together with iron and aluminum, on the other hand, that in the effluent the excess of EDTA can be readily titrated back by zinc acetate solution against xylenolorange indicator at pH 5,6, even if Ti is present. End point is just as sharp as in presence of iron+aluminum.

Consequently, titrating back the excess or EDTA in the effluent in presence of Fe+Ti+Al, one determines the quantity of EDTA equivalent to the sum of the three cations, and the method of analysis need not be modified because of the presence of Ti, at least as far as separation is concerned. The only difference is that we have to take into consideration, besides the expected amount of iron and aluminum, that of Ti as well, in order to assess approximately the amount of EDTA to be added to the solution for avoiding the use of an unnecessarily great excess:

b) *Possibilities of the determination of titanium in the effluent*

In his book PŘIBIL [1961] refers to one of I. SAJU's papers [1954] according to which Fe+Ti+Al can be determined in such a way that first the amount of 0,05 M EDTA equivalent to that of Fe+Ti+Al is determined by titrating back the excess of EDTA of known quantity added to the aliquot part of solution and then 10 ml of 10% diammonium hydrophosphate solution (containing per liter 20 ml hydrochloric acid of 1,12 Sp.g.) is added to the solution. A few minutes later, titanium precipitates in form of titanium phosphate and an equivalent amount of EDTA is released. This latter is, in turn, titrated back by 0,05 M zinc acetate solution and the amount of titanium is thus determined. Thereafter, 30 ml of saturated, neutral NaF solution is added to the solution, so that an amount of EDTA equivalent to aluminum is released, which is also titrated back by zinc acetate, determining in this way the amount of aluminum. The author referred to above observed a fluctuation around 0,2 mg of the values obtained while determining aluminum.

The above method was first tested on Ti solution. In doing so, to the solution with known Ti content 0,05 M EDTA was added in excess which was titrated back (see results of titration in Table 3), then the required diammonium hydrophosphate solution was added to the former and a few minutes later the amount of EDTA released, equivalent to Ti content, was titrated. The results are shown in Table 4.

TABLE 4.

Amount of titanium (TiO_2 mg) as determined by titrating back the amount of 0,05 M EDTA released on adding ammonium phosphate after back titration of the excess of 0,05 M EDTA.

TiO_2 mg calc.	In aliquot parts of stock solution	In aliquot part of solution passed through exchanger
1,95 mg	1,95 mg 1,99 1,95 1,95 1,96 mg +0,01	1,95 mg 1,91 1,87 1,83 1,89 mg —0,06
4,87 mg	4,91 mg 4,83 4,83 4,87 4,86 mg —0,01	4,83 mg 4,91 4,87 4,79 4,85 mg —0,02

The above analyses certainly suggest that if ammonium phosphate is added, exact results can also be obtained by titrating back the amount of EDTA released from the Ti-EDTA complex. We wonder, however, if similarly reliable results can be obtained in cases when both titanium and aluminum are present. For this very reason, we added the necessary excess of EDTA to aliquot parts of stock solution containing known amounts of aluminum, afterwards, at pH 5,6, we titrated back the excess by 0,05 M zinc acetate solution against xylenolorange indicator, determining thereby the amount of aluminum (see Table 5, values *a*). Thereafter, 15 ml of 10% solution of diammonium hydrophosphate was added to the solutions. As shown by Table 5, with increasing aluminum content, increasing amounts of EDTA were released

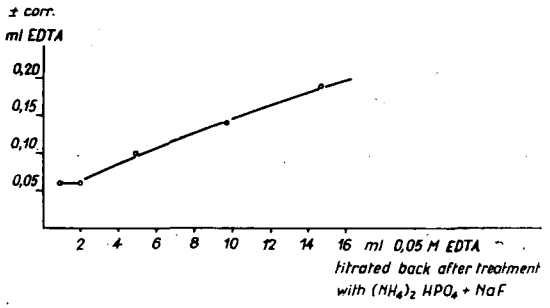
although no titanium was present. In other words, it seems that if both titanium and aluminum are present, the separation of titanium by ammonium phosphate and by titrating back of the released EDTA is not altogether unambiguous — at least not under the present experimental conditions —, as some aluminum is also precipitated and an equivalent amount of EDTA is also released, which are both titrated back during the back titration of the released amount of EDTA equivalent to Ti. The values x in Table 5 give the amounts of aluminum precipitated at an increasing rate with increasing aluminum content. The next step is to add 30 ml of saturated NaF solution to the former. Aluminum precipitates then as cryolite. The amount of aluminum is determined by titrating back the released amount of EDTA. The results are represented by values y in Table 5. As shown by these data, they fall short of the values a determined for Al by back titration of excess of EDTA, whereas the sum of the values $x+y$ show a very good agreement with both the calculated amounts of aluminum and the values a (determined by back titration of excess of EDTA). The differences between the values obtained by back titration and those calculated are, except for a few measurements, less than 0,1 mg, whereas the measured amounts (y) of aluminum fall by 0,15—0,30 mg short of the calculated values even in presence of 10—20 mg Al. This stands to reason, since this lacking amount of aluminum precipitated as early as during the treatment by ammonium phosphate and the equivalent amount of EDTA had already been titrated back, which, in turn, caused a + error in the determination of Ti. Presumably, this is the reason for the fluctuation of values around 0,2 mg, a fact pointed out in I. SAJO's paper, too.

TABLE 5.

Al computed	a	x	y	$x+y$	$x+y/a$ Δ	$x+y$/comp. Δ
		Al	in mg			
1,348	1,36	0,08	1,26	1,34	—0,02	—0,008
2,696	2,64	0,09	2,57	2,66	+0,02	—0,039
6,740	6,75	0,15	6,59	6,74	—0,01	0,000
13,480	13,40	0,19	13,21	13,40	0,00	—0,080
20,220	20,24	0,28	19,89	20,17	—0,07	—0,050
1,348	1,35	0,05	1,27	1,32	—0,03	—0,028
2,696	2,67	0,05	2,63	2,68	+0,01	—0,016
6,740	6,71	0,09	6,58	6,67	—0,04	—0,070
13,480	13,42	0,15	13,25	13,40	—0,02	—0,080
20,220	20,22	0,20	19,98	20,18	—0,04	—0,040
1,348	1,35	0,12	1,21	1,33	—0,02	—0,018
2,696	2,64	0,09	2,69	2,78	+0,18	+0,084
6,740	6,72	0,16	6,55	6,71	—0,01	—0,030
13,480	13,41	0,21	13,13	13,34	—0,07	—0,140
20,220	20,30	0,29	19,87	20,18	—0,12	—0,040

The values x and y and their divergences from values a and from the values computed, as shown in Table 5, suggest that during separation by ammonium phosphate some aluminum also precipitates together with titanium, and therefore the amount of EDTA released this time is greater than would

correspond to the actual titanium content (a positive error in Ti determination), and that just as much less is the amount of aluminum determined by back titration after precipitation by NaF (a negative error in Al determination). The aforementioned error increases with increasing amount of aluminum, as illustrated by Fig. 1, too. In this figure, we plotted, on the ordinate, those values of 0,05 M EDTA which had been released (amounts epuivalent to aluminum separated) on treatment by ammonium phosphate, while on the absciss we plotted the ammounts of 0,05 EDTA released on subsequent treatment by NaF. The sum of the two values is equivalent to the actual amount of aluminum present.



Error to be corrected in determining titanium and aluminum one after another

Considering the above, once Fe+Ti+Al (supplied into he effluent in the course of the applied set of analyses) are separated from the other cations, two possibilities offer themselves for determining separately the amount of iron, titanium, and aluminum.

The first one is that after the number of milliliters of 0,05 M EDTA equivalent to the total amount of the three cations present is determined by back titration of the excess of EDTA in the effluent, the excess is titrated back at pH 5,6 by 0,05 M solution of zinc acetate using xylenolorange indicator and to the solution 15 ml of 10% solution of diammonium hydrophosphate is added. After a few minutes of delay (pH being readjusted, if necessary, and some indicator added, again, to the solution), the amount of 0,05 M EDTA released is titrated. In presence of Al we take off therefrom the amount of correction dependent on the amount of Al, to be read off Fig. 1, so that the number of milliliters thus obtained will be equivalent to the amount of Ti present. Afterwards, 30 ml of saturated, neutral solution of NaF is added to the solution and the EDTA milliliters released are re-titrated at pH 5,6. The figure obtained being corrected as mentioned previously, we obtain the number of milliliters of 0,05 M EDTA equivalent to the actual amount of aluminum.

The second approach is that again the amount of 0,05 M EDTA corresponding to the total amount of Fe+Ti+Al is determined by back titration of the excess of EDTA in the effluent, but the effluent solution itself is not used for any further determinations. However, in the 50 ml aliquot taken from the original stock solution we determine, on the one hand, the iron content and the equivalent amount of 0,05 M EDTA, on the other hand, photometrically the amount of TiO_2 present and that of 0,05 M EDTA corresponding to it. Afterwards, these milliliter values are taken off, one by one, from those of

0,05 M EDTA determined earlier equivalent to the sum of Ti+Al+Fe and the amount of aluminum is thus obtained.

These facts are so much the more worth of consideration, as the analytical process hitherto developed applies not only to manganese ores in which the presence of either iron, or titanium, or aluminum (particularly that of these latter two) is merely incidental due to admixture of various accessory minerals, but it can be used for the analysis of rocks as well. And, as regards these latter, here we always must reckon with aluminum and titanium contents higher than in the case of manganese ores. Still, the higher the aluminum content, the greater the error.

CONCLUSIONS

1. In the analysis of manganese ores the zinc content can well be separated from the other components, if the solution (0,5 N for HCl) is percolated through the anion exchanger Amberlite IRA—400 and if afterwards the column is washed with 0,5 N hydrochloric acid. The effluent will contain the other cations which can be separated from each other on cation exchanger Wofatit KPS- 200 by using the techniques developed earlier. Using ammonium-ammoniumchloride solution, zinc can be eluted from the anion ecxhanger and immediately titrated in the eluate. The column can be regenerated by 0,5 N hydrochloric acid.

2. *a)* The analytical process using ion exchangers developed for the separation of Fe-Al-Mn-Ca-Mg can be applied in presence of titanium, too, as Ti will completely pass into the effluent solution, together with iron and aluminum.

b) The sum of the amounts of iron+titanium+aluminum in the effluent can be exactly determined by back titration of the excess of EDTA, at pH 5,6, using zinc acetate solution against xylenolorange indicator.

c) The sum of iron+titanium+aluminum and the equivalent amount of 0,05 M EDTA, respectively, in the effluent being known, we can determine each of them successively. First Ti is determined by separating with ammonium phosphate and measuring the amount of EDTA released, then aluminum by separating with NaF and titrating the equivalent EDTA released according to I. SAJO's method, with the difference that titration is performed at pH 5,6 and xylenolorange is used as indicator. However, as shown by our measurements, in successive determinations increasing aluminum content is accompanied by increasing error. In fact, titanium contents greater and aluminum contents smaller than the actual amount are determined. At Al contents of 2—3 mg the error is still negligible, but in presence of 20 mg of Al it is as great as 0,3 mg. The use of corrections permits to eliminate the error and the results thus obtained are already satisfactory. The divergence of the corrected aluminum contents from the computed ones is -0,039 mg, in the mean.

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REFERENCES

AMIN, A. M., FARAH, J. M. [1955]: Chemist Analyst, Vol. *44.* p. 65.

GRASSELLY, GY. [1962]: Analytical Methods of Manganese Ores I.—Acta Miner. Petr. Univ. Szegediensis, Tom. *XV.* pp. 7—18.

JENTZSCH, D., FROTSCHER, I. [1954]: Anwendung von Ionenaustauschern in der analytischen Chemie. II. Mitt. — Z. f. anal. Chemie, Bd. *144.* pp. 17—25.

PŘIBIL, R. [1961]: Komplexone in der chemischen Analyse. VEB Deutscher Verlag der Wissenschaften, Berlin.

SAJÓ, I. [1954]: Magyar Kémiai Folyóirat, *60.* 268, 331.

WILKINS, DONALD, H. [1959]: The Determination of Nickel, Cobalt, Iron and Zinc in Ferrites. — Anal. Chim. Acta, Vol. *20.* pp. 271—273.

ANALYTICAL METHODS OF MANGANESE ORES III.

Contribution to the determination of Na_2O and K_2O in manganese ores

by

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The determination of alkali content may be of interest and necessary, whether natural manganese ores or artificial oxides are studied. On the one hand, various natural manganese compounds may contain alkali metals, such as potassium contained in cryptomelane, but alkali metals as adsorbed cations may be contained in various manganoxihydrates, particularly in those precipitated in colloidal state. On the other hand, alkali, especially potassium, may be present in various artificial manganese dioxides in dependence on the production technique adopted.

In rapid methods of silicate analysis the alkali content is usually determined by flame-photometry. L. SHAPIRO and W. W. BRANNOCK [1956] determined the alkali metals without preliminary separation, using lithium sulphate as internal standard. J. P. RILEY [1958] removed the interfering Fe, Al, Ti ions by means of an anion exchanger Amberlite IRA—400 in its citrate form, where ammonium sulphate was added as buffer to both the sample solutions and the standard solutions. In the book of selected papers compiled by A. A. SMALES and L. R. WAGER [1960], E. A. VINCENT has proposed separation of interfering ions by ammonium hydroxide and ammonium carbonate. This method was applied by M. WEIBEL [1961], too, in his rapid process of rock analysis.

In view of the rather ample choice of methods available the only question we faced concerned the choice of the basic approach which would yield reliable results in a comparatively simple way in the analysis of manganese ores, i.e. in presence of considerable amounts of manganese.

EXPERIMENTAL

The determinations were carried out by means of Zeiss Flammenphotometer Modell III „A". Comparing the different methods for determination of Na_2O and K_2O, we found simple and, at the same time, reliable the method proposed by VINCENT and WEIBEL. Slightly modified (chiefly as far as the attacking and, in certain respect, the measuring techniques are concerned), it yields accurate results even at considerable manganese contents, as demonstrated by the analyses to be shown later in this paper.

I. Dissolution of the sample

1. 0,5 g of finely powdered manganese ore is weighed into a 250 ml beaker, 25 ml of 1:1 hydrochloric acid and a few drops of 30% hydrogen hyperoxide is added to the sample. The beaker is covered and slightly heated over a water bath. If after the cessation of effervescence some undissolved brownish-blackish grains are still visible at the bottom of the beaker, a few drops of hydrogen hyperoxide are added to the solution.

2. As the sample is completely dissolved and dark grains are no longer visible at the bottom of the beaker, the solution is brought to boil, and after a few minutes of boiling it is thoroughly washed into a platinum dish of suitable size, together with the possible insoluble residue. Afterwards, it is almost completely evaporated on a water bath.

3. 1 ml of 60% perchloric acid and 15 ml of 40% hydrofluoric acid is poured into the platinum dish (to dissolve the insoluble, silicate-bearing residue) and the hydrofluoric acid is expelled over a water bath. In case of considerable amounts of insoluble residue this latter operation is repeated by adding 15 ml of hydrofluoric acid.

4. After the removal of hydrofluoric acid the residue is moistened merely by perchloric acid. The platinum dish is put on a sand bath and most of perchloric acid is removed by careful heating. Once it is done, the dish is taken off from the sand bath, but do not allow to become completely dry.

5. After the second removal of perchloric acid, 1 ml of perchloric acid is poured into the platinum dish and some hot water is added to it, in order to dissolve the residue. Complete dissolution of the residue is achieved by washing thoroughly the contents of the platinum dish into a 100 ml beaker repeating this operation several times, taking care that the volume of the solution should not exceed 60—70 ml. The solution is then boiled for a short time.

6. After cooling the solution is transferred into a 100-ml graduated flask and filled up to the mark with ion-free water.

The alkali content is determined in aliquot parts taken from this solution by flame photometry. The volume of the aliquot parts taken depends on the alkali content to be expected.

II. Reagents and solutions

1. Stock solutions

A. Stock solution of NaCl: 0,9430 g of NaCl dried at 105 °C and 0,7920 g of KCl dried at 105 °C are weighed. Having been dissolved, they are poured into a calibrated 1000 ml measuring flask filled up to the mark with ion-free water: 1 ml of solution = 0,5 mg Na_2O + 0,5 mg K_2O. The solution is stored in a plastic vessel.

B. Ammoniacal-ammonium carbonate solution: 2 g of ammonium carbonate is dissolved in 100 ml of ammonium hydroxide diluted 1 : 9. Each time a fresh solution has to be prepared.

C. Blank test solution.

C_1. *Concentrated:* 1 ml of perchloric acid is poured into a 100 ml measuring flask and diluted by ion-free water up to the mark.

C_2. *Diluted:* 10 ml of concentrated blank test solution *(C_1)* (=0,1 ml of perchloric acid) is brought into a 100 ml measuring flask, diluted by water to 50—60 ml, added to it 5 ml of ammoniacal ammonium carbonate solution *(B)* and filled up with ion-free water up to the mark.

2. Preparation of the standard solutions

a) 1, 2, 4, 6, 8, 10 ml volumes of stock solution *A* are successively introduced into 100 ml graduated flasks (0,5, 1, 2, 3, 4, 5 mg Na_2O and K_2O, respectively).

b) 10 ml of concentrated blank test solution *(C_1)* is poured into each flask, being diluted to 50—60 ml.

c) The flasks are charged with 5 ml of ammonia-ammonium carbonate solution each, shaken up, and filled up to the mark with ion-free water. Afterwards, they are thoroughly shaken up once more, and the solution with precipitate is poured over into a plastic bottle (dry) provided with a well-sealing cover, where it is let stay for one day.

III. Determination of Na_2O and K_2O

1. Volumes corresponding to the alkali content expected are taken with a pipette or burette from 100-ml sample stock solution obtained following the attack, and each is poured into a 100 ml measuring flask.

Since in the above standard Na+K solution series the extreme values of the alkali concentration are 0,5 mg/100 ml and 5,00 mg/100 ml Na_2O or K_2O, respectively, it is advisable to take such aliquot parts from the stock solution that their alkali content should fall within these two limits.

2. To the aliquot parts of stock solution poured into the flask and filled up to 50—60 ml with water add 5 ml of ammoniacal ammonium carbonate solution, mixed well, and filled up to the mark with ion-free water, then after repeated mixing the solution with the precipitate is poured over into a dry plastic bottle provided with a well-sealing cover, where it is let stay for one day, just as was the case with the standard solutions.

3. Using Na filter, the members of the standard solution and afterwards the sample solutions are atomized, one by one, into the flame. The atomization of the standard solutions and of the sample solutions is repeated alternately at least three times. In the further course of the analytical process the mean values of galvanometer readings are taken and then plotted.

After the atomization of the individual samples it is the diluted blank test solution *(C_2)* that will be atomized and the values of the corresponding readings are discounted from those of both the calibrational series and the samples analysed.

From the plastic bottle the clear solution above the precipitate is atomized. The precipitate itself need not be filtrated previously, we must merely take care that the precipitate should not be stirred up to avoid precipitate particles entering the atomizer.

4. After the determination of Na_2O, filter K is introduced and the K_2O content is determined in just the same way as previously and galvanometer readings proportional to K concentrations are taken.

5. The readings obtained for the members of the standard series are plotted in form of a calibration curve. Superimposing on the latter the galvanometer readings of the individual samples, we can determine the Na_2O and/or K_2O content.

IV. Precision and accuracy of determination

Following the above-outlined working process, we made first parallel determinations of the alkali content of a granite sample, then having attacked the same rock sample in one and the same way and having prepared the stock solution, we added different amounts of manganese to the solution to be atomized, before filling it up, and we performed the determination of the alkali content of this solution, too. The results are shown in Table 1.

TABLE 1.

Na_2O and K_2O contents of a standard rock sample as obtained by parallel measurements of the original sample and as determined in presence of different amounts of manganese

Na_2O % as determined					K_2O % as determined					Mn added mg/100 ml
in the original sample		in the same, but in presence of Mn			in the original sample		in the same, but in presence of Mn			
4,00	3,98	4,00	3,84	3,90	3,40	3,56	3,54	3,51	3,38	0,53
4,00	3,82	4,00	3,84	3,90	3,40	3,52	3,54	3,52	3,45	1,07
3,99	4,17	4,00	3,84	3,92	3,40	3,48	3,52	3,51	3,40	2,14
3,99	3,82	4,00	3,84	3,90	3,40	3,47	3,52	3,55	3,45	5,35
3,92	3,90	4,00	3,82	3,89	3,40	3,40	3,50	3,52	3,46	10,71
3,92		3,98	3,79	3,86	3,40		3,60	3,55	3,45	21,42
3,98		3,98	3,80	3,85	3,56		3,60	3,48	3,45	42,84
$x=3,95\%$		$x=3,90\%$			$x=3,44\%$		$x=3,50\%$			
$s=\pm 0,0822$		$s=\pm 0,0743$			$s=\pm 0,0666$		$s=\pm 0,0567$			
$s_{\bar{x}}=0,0237$		$s_{\bar{x}}=0,0162$			$s_{\bar{x}}=0,0164$		$s_{\bar{x}}=0,0123$			
$C=2,08$		$C=1,90$			$C=1,93$		$C=1,62$			
$E=0,60$		$E=0,41$			$E=0,559$		$E=0,353$			

The terminology of the parameters characterizing the accuracy of determination is the same as that applied in the author's first paper on manganese ore analysis [GRASSELLY, 1962], viz.: x=mean; s=standard deviation; $s_{\bar{x}}$ = standard error; C=relative deviation, and E=relative error.

In one of their paper FAIRBAIRN et al. [1951] have dealt with the precision and accuracy of different methods of rock analysis, relying on analyses from various laboratories. A similar comparative study of 16 parallel silicate analyses is reported by G. CSAJÁGHY [1959]. Here we have used only the data concerning alkali content in the references quoted. A comparison of FAIRBAIRN's and CSAJÁGHY's data concerning the accuracy of alkali determinations to those obtained by us in presence of considerable amounts of manganese indicates that the present analytical process provides reliable, accurate results even at high manganese contents and that it can certainly be applied successfully for the determination of the alkali content of manganese ores.

TABLE 2

Precision of the determination of Na_2O and K_2O

In rocks				In rocks in presence of manganese	
as checked by the data of					
FAIRBAIRN		CSAJÁGHY		the author	
	Na_2O	Na_2O	K_2O	Na_2O	K_2O
x	3,26	5,51	3,21	4,42	3,90	3,50
s	0,284	0,549	0,173	0,218	0,082	0,056
$s_{\bar{x}}$	0,06	0,11	0,043	0,054	0,016	0,012
C	8,71	9,96	5,39	4,93	1,90	1,62
E	1,81	2,07	1,35	1,23	0,41	0,35

CONCLUSIONS

Manganese ores can be advantageously analysed for Na_2O and K_2O by using, with slight modification, the method proposed by VINCENT and WEIBEL which essentially consists in separating the interfering ions by ammoniacal ammonium carbonate solution and determining subsequently the alkali content by flame photometry directly from the solution without filtering the precipitate. The manganese ores (either oxides or carbonates) are dissolved by hydrochloric acid adding to it a few drops of hydrogen hyperoxide or, provided some insoluble silicate residue is present, the attack by hydrochloric acid is followed by an attack by hydrofluoric acid — perchloric acid. The present analytical process yields accurate results even in presence of considerable amounts of manganese. And since the determination of the alkali content does not require to remove the disturbing ions by means of exchangers or to filter the precipitate, it can be performed in a simple way and relatively quickly, if only the actually necessary operations are considered (in fact, the precipitate is let stay for a night). In case of serial measurements, on one day the dissolution of the samples and the preparation of the solutions are performed, and on the following day we may proceed to measure the alkali content of the solutions prepared the day before.

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REFERENCES

CSAJÁGHY, G. [1959]: Szilikátelemzéseink megbízhatósága. — Ann. Report of the Hung. Geol. Inst. of 1955 and 1956. pp. 21—28.

FAIRBAIRN, H. W., SCHLECHT, W. G., STEVENS, R. E., DENNEN, W. H., AHRENS, L. H., CHAYES, F. [1951]: A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks. — U. S. Geol. Survey Bull. *980*.

GRASSELLY, GY. [1962]: Analytical Methods of Manganese Ores I. — Acta Miner. Petr. Univ. Szegediensis, Tom. *XV*. pp. 7—18.

RILEY, J. P. [1958]: The Rapid Analysis of Silicate Rocks and Minerals. — Anal. Chim. Acta. *19*. pp. 413—428.

SHAPIRO, LEONARD, BRANNOCK, W. W. [1956]: Rapid Analysis of Silicate Rocks. — U. S. Geol. Survey Bull. *1036—C*. pp. 19—56.

SMALES, A. A., WAGER, L. R. [1960]: Methods in Geochemistry. Interscience Publishers, London, Chapter 3. VINCENT, E. A.: Analysis by Gravimetric and Volumetric Methods. Flame photometry, Colorimetry and Related Techniques. pp. 33—80.

WEIBEL, M. [1961]: Die Schnellmethoden der Gesteinsanalyse. — Schweiz. Miner. Petr. Mitt. *41*. pp. 285—294.

BEITRÄGE ZUR KENNTNIS DER OBERPALÄOZOISCHEN UND UNTERMESOZOISCHEN SPOREN-POLLENGESELLSCHAFTEN IN UNGARN

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EINLEITUNG

Nach den palynologischen Untersuchungen der mangancarbonatischen Schichten in Urkut tauchte der Gedanke auf, daß diese Schichten nach den jetzigen Auffassungen aus dem mittleren und nicht aus dem unteren Jura stammen könnten. Um die palynologischen Kenntnisse über das Manganerz und zugleich über die einheimischen mesozoischen Ablagerungen zu erweitern, wurden in verschiedenen Gebieten ergänzende Untersuchungen durchgeführt.

Aus der Sporen-Pollengemeinschaft des in der Bohrung So—72 erreichten Grundgebirges des Doroger Braunkohlenbeckens ergaben sich für die Stratigraphie beachtenswerte, Daten, die es verdienen, bekannt gegeben zu werden.

MATERIAL UND METHODE

Das Untersuchungsmaterial stammt aus der Bohrung So—72, und zwar aus einer Tiefe von 575,10—576,40 m. Eine beträchtliche Anzahl der beobachteten Sporomorphen ist zerstört. Sie entzog sich somit einer genauen Bestimmung. Mehrere in der Literatur bisher noch nicht beschriebene Formgattungen und -arten sind aufgefallen. Sie sollen aber nicht besprochen werden, weil sie schlecht erhalten sind und zu selten vorkommen. Die aus der Literatur entnommenen Angaben zur Stratigraphie der beobachteten Pollentypen bilden die Grundlage für die Altersbestimmung des Grundgebirges.

ERGEBNISSE

Sporen konnten nur in kleiner Zahl und mit wenig Typen beobachtet werden. Zu nennen sind

Punctatisporites fsp., Taf. I; 1, 2

Trilites fsp., Taf. I; 3, 4

Toroisporis (Toroisporis) fsp., Taf. I; 5, 6

In der Sporomorphengemeinschaft dominieren die Pollentypen von Gymnospermen. Von den Formen ohne Luftsack erschien nur ein Typ *(Spheripollenties* cf. *subgranulatus* COUPER 1958, Taf. II; 7, 8), und ganz ähnlich ist der monosaccate Typ auch nur durch eine Form repräsentiert *(Enzonalasporites* fsp., Taf. I; 7, 8). In der Sporomorphen-Gemeinschaft wird die überwiegende Mehrzahl von solchen Pollen gestellt, die sich in die Gruppe der *Disaccites* einreihen lassen. Auch die Zahl der Typen ist hier verhältnismäßig groß. Im Untersuchungsmaterial kamen vor

drei Formen von *Limitisporites,* Taf. II; 15, 16; Taf. III; 9—12; 21—24
eine Form von *Pallidosporites,* Taf. III; 29—32
drei nicht näher bestimmbare Formen von *Falcisporites,* Taf. II; 9, 10, 13, 14; Taf. III; 25—28
eine Form von *Alisporites,* Taf. II; 11, 12
eine evtl. ebenfalls zu Alisporites gehörige Form, Taf. I; 19, 20
eine Form von *Pityosporites,* Taf. I; 21, 22
zwei nicht näher bestimmbare Formen von *Striatites,* Taf. III; 13—16, Taf. III; 17—20
drei evtl. zu *Falcisporites* gehörige Form, Taf. II; 9, 10, Taf. II; 13, 14, Taf. III; 25—28
eine von *Vitreisporites,* Taf. II; 1, 2
zwei nicht bestimmbare von *Vesicaspora,* Taf. II; 3, 4, 5, 6 und
vier Formen von *Unatextisporites* (in neuerer Zeit *Ovalipollis* genannt), Taf. I; 9—18.

Außer diesen konnten noch einige neue disaccate Typen beobachtet werden, deren Gattungszugehörigkeit noch unklar ist. Man kann sie nach mehreren Haupttypen und einem Untertyp ordnen, wobei die Haupttypen etwa den taxionomischen Rang von Formgattungen einnehmen (Taf. II; 17—28; Taf. III; 1—8, 33—36).

FOLGERUNGEN

Nach den aus der Literatur bekannten stratigraphischen Daten für die genannten Typen muß die Pollengemeinschaft ein Perm-Trias-Übergangsgepräge besitzen. Ältere, in erster Linie die Perm-Zeit charakterisierende Elemente sind die *Limitisporites, Pallidosporites, Striatites, Falcisporites, Alisporites* und die unbekannten disaccaten Pollen.

Hinsichtlich ihrer Grundmorphologie gleichen sie den in Zechsteinablagerungen nachgewiessenen Formen von SCHAARSCHMIDT [1963]. Dagegen sind die Formgattungstypen von *Unatextisporites, Vitreisporites* und auch von *Enzonalasporites* hauptsächlich in der Trias und im Jura verbreitet.

Die bisher vorliegenden Ergebnisse aus der Bearbeitung paläozoischer und älterer mesozoischer Sporomorphen-Gemeinschaften Ungarns lassen nun folgende Aussagen zu:

1. Die älteste bewertbare Sporen-Pollen-Gemeinschaft (Oberperm, Zech-

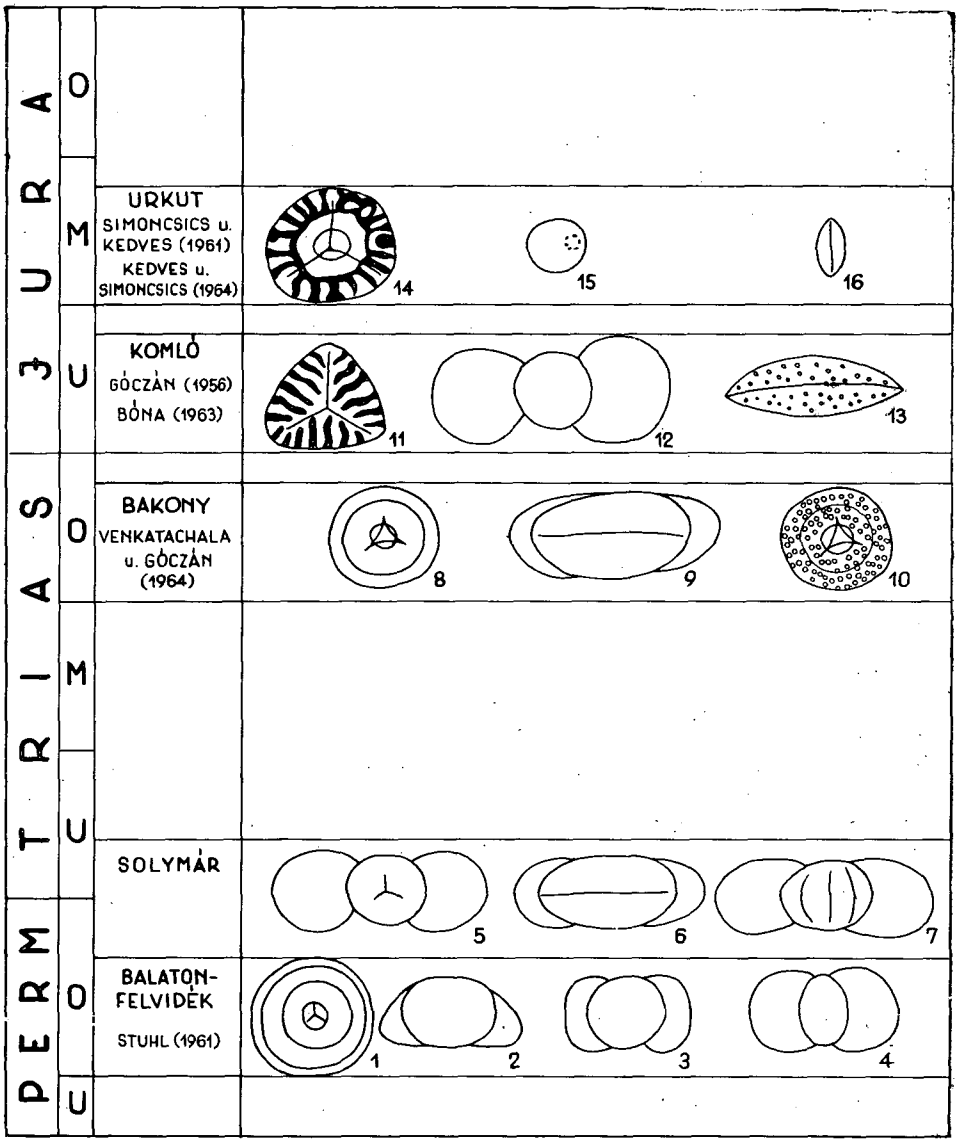


Abb. 1

Schemen von einigen charakteristischen Sporomorphen-Typen aus den oberpaläozoischen und mezozoischen Sporen-Pollen-Gemeinschaften in Ungarn: 1. *Nuskoisporites dulhuntyi*, 2. *Pityosporites schaubergi*, 3. *Pityosporites zapfei*, 4. *Pityosporites delasaucei*, 5. *Limitisporites* fsp., 6. *Unatextisporites* fsp., 7. *Disaccites* II (fgen. et fsp. indet.), 8. *Circulina* fsp., 9. *Unatextisporites* fsp. (=*Ovalipollis* fsp.), 10. *Granuloperculatipollis* fsp., 11. *Zebrasporites* fsp., 12. „*Podocarpus*-Typen", 13. *Bennettitinae*-Pollen-Typen („*große monosulcate*" Formen), 14. *Staplinisporites* fsp. (*hungaricus*-Type), 15. *Spheripollenites* fsp., 16. *Monosulcites* fsp. (*minor*- und *urkutiensis*-Typen).

stein) ist aus der Arbeit von STUHL [1961] bekannt. In dieser Gemeinschaft dominieren die zu den *Disaccites* gehörenden Pollentypen. Für die Alterseinstufung wichtig sind *Nuskoisporites dulhuntyi* POT. & KLAUS, wegen ihrer Häufigkeit auch *Pityosporites schaubergi* POT. & KLAUS, *Pityosporites zapfei* POT. & KLAUS und *Pityosporites delasaucei* POT. & KLAUS. Bei diesem Komplex ist jedoch in Betracht zu ziehen, daß er von festländischen Ablagerungen stammt und daß der Erhaltungszustand der Formen nicht gut ist.

2. Über diese Gesellschaft in den Grenzbereich zwischen Perm und Trias setzen wir die in dieser Arbeit vorgestellte Sporomorphenflora aus der Bohrung So–72.

Der Mangel an *Nuskoisporites dulhuntyi* POT. & KLAUS und anderseits der Formenreichtum der *Unatextisporites*-Gruppe läßt eine klare Abtrennung dieser jüngeren von der älteren Flora aus dem oberen Perm zu.

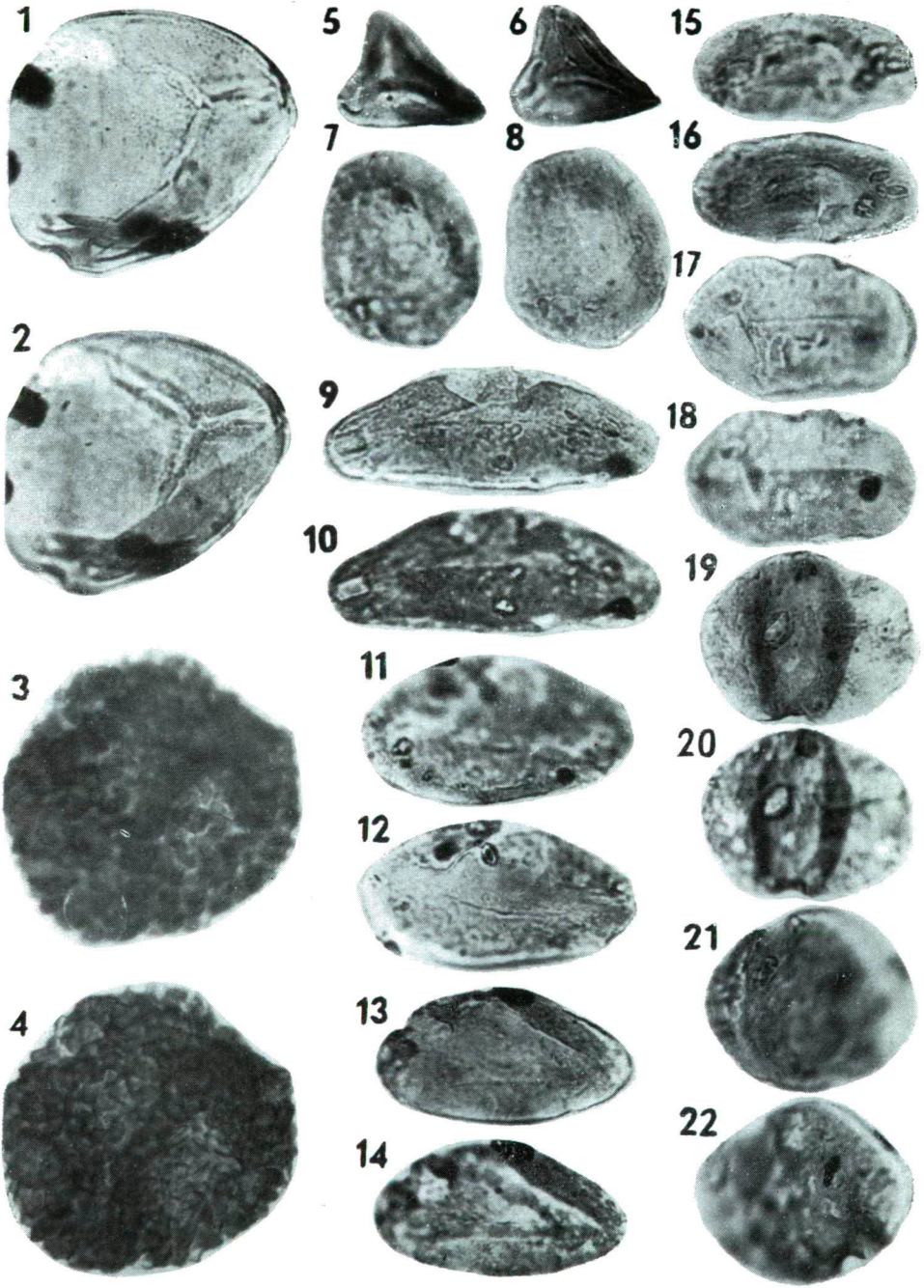
3. Sporomorphen-Gemeinschaften aus der Unter- und Mitteltrias sind in Ungarn noch unbekannt. Nach VENKATACHALA & GÓCZÁN [1964] sind die Ablagerungen der Obertrias aus dem Bakony-Gebirge reich an neueinsetzenden Typen von Gymnospermenpollen. Charakteristisch ist die verhältnismäßig hohe Zahl von Vertretern der *Operculati*-Gruppe *(Classopollis, Circulina, Granuloperculatipollis)* und *Ovalipollis* (cf. *Unatextisporites).*

4. Die unterliassische Steinkohle von Komló ist nach den Angaben von GÓCZÁN [1956] und BÓNA [1963] von der vorigen Gemeinschaft gut unterscheidbar. Also dürften zwischen dem von VENKATACHALA & GÓCZÁN [1964] beschriebenen Komplex und dem Komloer Typ noch weitere Übergangs-Pollengemeinschaften zu erhoffen sein. Die Steinkohle ist reich an Classopollis-Pollen, wie sie auch im Urkuter Mangan mit hohen Prozentwerten vorkommen. Kennzeichnend sind weiterhin eine *„große monosulcate"* Form, die Formenmannigfaltigkeit des *„Podocarpus"*-Typs, der im Urkuter Mangan fehlt, und der Nachweis von *Zebrasporites*. Letzterer wird an der Grenze von der Trias zum Jura häufig gefunden (cf. SCHULZ, [1962]) ist aber auch im unteren Jura noch verbreitet.

Die Sporomorphengesellschaft des Urkuter Manganerzes steht in scharfem Gegensatz zu der aus dem Komloer unteren Jura. Es fehlen die *„Podocarpus"*-Typen, die als altertümliche disaccate Pollenform zu betrachten sind. Dies ist insofern von Bedeutung, als sich die durch den Wind antransportierten Luftsackpollen auf der offenen Wasserfläche des Manganerzsammlers viel leichter

Tafel I

Fig. 1, 2. — *Punctatisporites* fsp., So—72—T—2, 15,2/109,2.
Fig. 3, 4. — *Trilites* fsp., So—72—T—1, 21,3/107,4.
Fig. 5, 6. — *Toroisporis* (Toroisporis) fsp., So—72—T—1, 5,6/108,3.
Fig. 7, 8. — *Spheripollenites cf. subgranulatus* COUPER 1958, So—72—T—1, 22,2/103,2,
Fig. 9, 10. — *Unatextisporites* fsp.$_1$, So—72—T—3, 8,5/107,7.
Fig. 11, 12. — *Unatextisporites* fsp.$_2$, So—72—T—3, 21,6/102,5.
Fig. 13, 14. — *Unatextisporites* fsp.$_2$, So—72—T—1, 17,6/118,7.
Fig. 15, 16. — *Unatextisporites* fsp.$_3$, So—72—T—1, 16,7/105,4.
Fig. 17, 18. — *Unatextisporites* fsp.$_4$, So—72—T—1, 17,6/117,2.
Fig. 19, 20. — *Cf. Alisporites* fsp., So—72—T—2, 17,8/117,5.
Fig. 21, 22: — *Pityosporites* fsp., So—72—T—1, 17,8/114,2.
500×.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anhäuften als in der geschlossenen Vegetation des Strauchmoores, wo nach bisherigen Vorstellungen die Tanne als die Lieferantin von Luftsackpollen extrapalustrischen Charakter besaß. Das Urkuter Mangan läßt sich auch wegen der Häufigkeiten von *Staplinisporites*, *Spheripollenites* und *Monosulcites* palynologisch von der Komloer Steinkohle absondern.

Beim Überblick über das Ganze ergibt sich als Schlußfolgerung, daß die beträchtlichen Unterschiede zwischen den einzelnen Komplexen ihre Ursache in größeren Zeitdifferenzen haben müssen. Ausnahmen bilden höchstens die Oberperm- und die Perm/Trias-Gesellschaften. Eine andere Frage ist dagegen, wie groß der Zeitsprung zwischen der Komloer Steinkohle und dem Urkuter Mangan wirklich gewesen ist. Vorläufig wird die Komloer Steinkohle in den unteren Teil und das Urkuter Mangan in den oberen Teil des unteren Jura gestellt. Nach unseren bisherigen palynologischen Ergebnissen kommt jedoch als Alter für das Manganerz eher der mittlere Jura infrage, worauf wir schon an einigen Stellen hingewiesen haben und wofür auch einige bestätigende Daten zur Verfügung stehen.

LITERATUR

BALME, B. E. and HENNELLY, J. P. F. [1955]: Bisaccate Sporomorphs from Australian Permian Coals. — Austr. J. Bot. *3*. 89—98.

BALME, B. E. and HENNELLY, J. P. F. [1956]: Monolete, Monocolpate, and Alete Sporomorphs from Australian Permian Sediments. — Austr. J. Bot. *4*. 54—67.

BÓNA, J. [1963]: Palynologische Untersuchungen zwecks einer Fernkorreliernug der liassischen Steinkohlenflöze des Mecsek-Gebirges. — Földt. Közl. *93*. 15—23.

DÖRING, H. [1964]: Trilete Sporen aus dem Oberen Jura und dem Wealden Norddeutschlands. Geologie. *13*. 1099—1130.

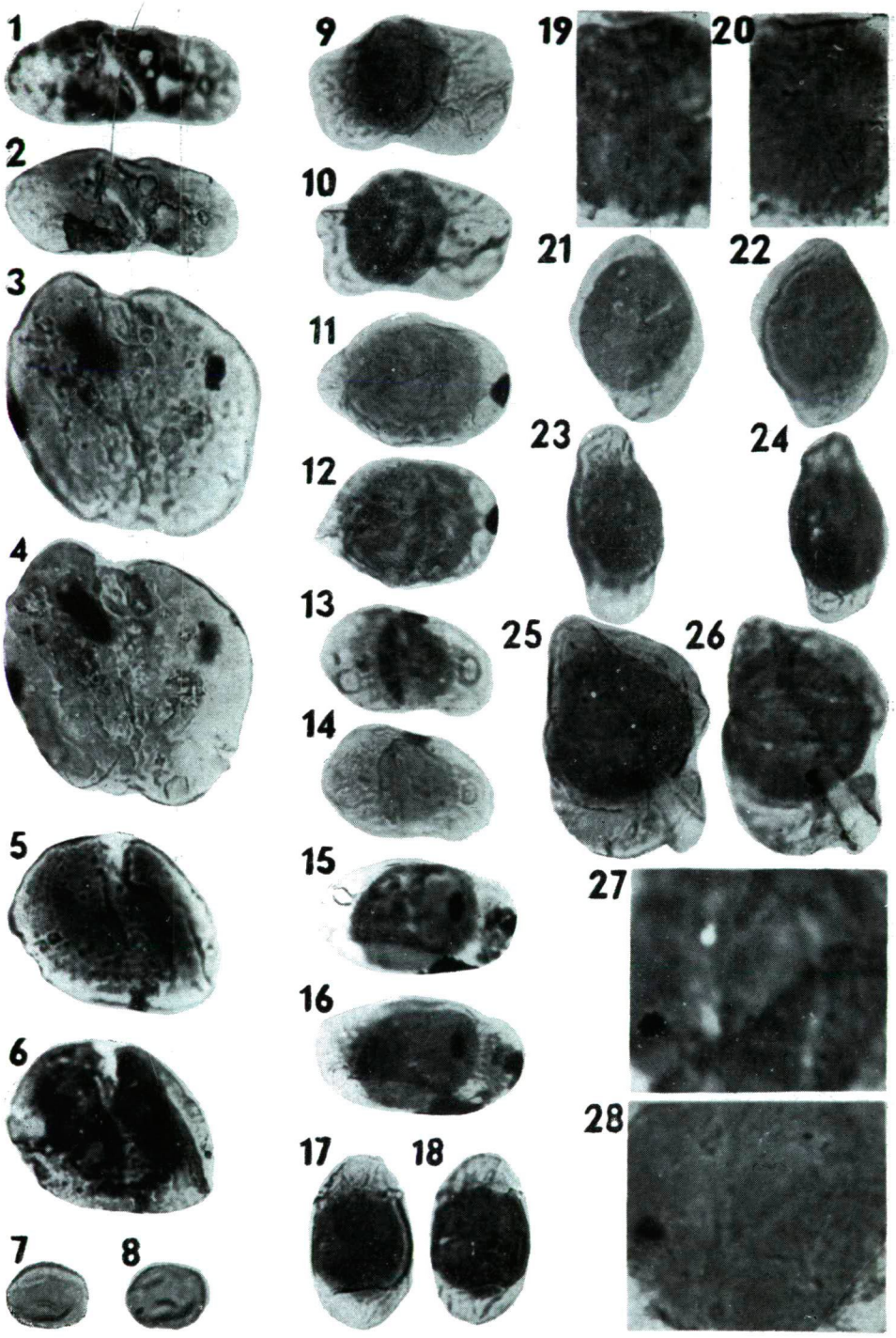
GÓCZÁN, F. [1956]: Pollenanalytische (palynologische) Untersuchungen zur Identifizierung der liassischen Schwarzkohlenflöze von Komló. — M. Áll. Földt. Int. Évkönyve. *45*. 167—212.

GREBE, H. [1957]: Zur Mikroflora des niederrheinischen Zechsteins. — Geol. Jb. *73*. 51—74.

JANSONIUS, J. [1962]: Palynology of Permian and Triassic sediments, Peace River area, Western Canada. — Palaeontographica. B. *110*. 35—98.

Tafel II

Fig. 1, 2. — *Vitreisporites* fsp., So—72—T—1, 4,8/106,3, 500×.
Fig. 3, 4. — *Cf. Vesicaspora* fsp.$_1$, So—72—T—1, 15,8/118,2, 500×.
Fig. 5, 6. — *Cf. Vesicaspora* fsp.$_2$, So—72—T—1, 9,5/102,3, 500×.
Fig. 7, 8. — *Spheripollenites cf. subgranulatus* COUPER 1958, So—72—T—1, 22,2/103,2, 500×.
Fig. 9, 10. — *Cf. Falcisporites* fsp.$_1$, So—72—T—1, 19,9/115,8, 500×.
Fig. 11, 12. — *Alisporites* fsp.$_1$, So—72—T—1, 19,2/108,3, 500×.
Fig. 13, 14. — *Cf. Falcisporites* fsp.$_2$, So—72—T—1, 20,3/104,8, 500×.
Fig. 15, 16. — *Limitisporites* fsp.$_1$, So—72—T—5, 4,6/102,3, 500×.
Fig. 17, 18. — *Disaccites* I/1, So—72—T—2, 17,2/108,2, 500×.
Fig. 19, 20. — *Disaccites* I/1, So—72—T—2, 17,2/108,2, 1000×.
Fig. 21, 22. — *Disaccites* I/2, So—72—T—1, 22,1/103,2, 500×.
Fig. 23, 24. — *Disaccites* I/3, So—72—T—1, 18,2/115,4, 500×.
Fig. 25, 26. — *Disaccites* II, So—72—T—1, 9,4/118,6, 500×.
Fig. 27, 28. — *Disaccites* II, So—72—T—1, 9,4/118,6, 1000×.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KEDVES, M. and SIMONCSICS, P. [1964 a]: Microstratigraphy of the carbonate manganese ore layers of the shaft III of Úrkút on the basis of palynological investigations. — Acta Miner.-Petr. Szeged. *16*. 3—48.

KEDVES, M. et SIMONCSICS, P. [1964 b]: Spores nouvelles extraites de minerai de manganèse Jurassique de la région d'Úrkút (Hongrie). — Pollen et Spores. *6*. 605—610.

KLAUS, W. [1955]: Über die Sporendiagnose des deutschen Zechsteinsalzes und des alpinen Salzgebirges. — Z. deutsch. geol. Ges. *105*. 776—788.

KLAUS, W. [1960]: Sporen der karnischen Stufe der ostalpinen Trias. — Jb. Geol. B. A. *5*. 107—183.

KLAUS, W. [1963]: Sporen aus dem südalpinen Perm. — Jb. Geol. B. A. *106*. 229—263.

KRÄUSEL, R. und LESCHIK, G. [1955]: Die Keuperflora von Neuewelt bei Basel, II. Die Iso- und Mikrosporen. — Schweizerische Paläont. Abh. *72*. 1—70.

KRUTZSCH, W. [1955]: Über eine liassische „angiospermide" Sporomorphen. — Geologie. *4*. 65—76.

LESCHIK, G. [1956]: Sporen aus dem Salzton des Zechsteins von Neuhof (bei Fulda). — Palaeontographica. B. *100*. 122—142.

POTONIÉ, R. und KLAUS, W. [1954]: Einige Sporengattungen des alpinen Salzgebirges. — Geol. Jb. *68*. 517—546.

ROGALSKA, M. [1954]: Spore and pollen analysis of the Liassic coal of Blanowice in Upper Silesia. — Bull. Inst. Geol. Warsaw. *89*. 1—46.

SCHAARSCHMIDT, F. [1963]: Sporen und Hystrichosphaerideen aus dem Zechstein von Büdingen in der Wetterau. — Palaeontographica. B. *113*. 38—91.

SCHULZ, E. [1962]: Sporenpaläontologische Untersuchungen zur Rhät—Lias—Grenze in Thüringen und der Altmark. — Geologie. *11*. 308—319.

SIMONCSICS, P. and KEDVES, M. [1961]: Paleobotanical examinations on manganese series in Urkut (Hungary, Transdanubia). — Acta Miner. — Petr. Szeged. *14*. 27—57.

STANLEY, A. and POCOCK, J. [1962]: Microfloral analysis and age determination of Strata at the Jurassic—Cretaceous boundary in the Western Canada Plains. — Palaeontographica. *B. 111*. 1—95.

STUHL, Á. [1961]: Ergebnisse von Sporenuntersuchungen an den Permablagerungen des Balatonhochlandes. Földt. Közl. *91*. 405—412.

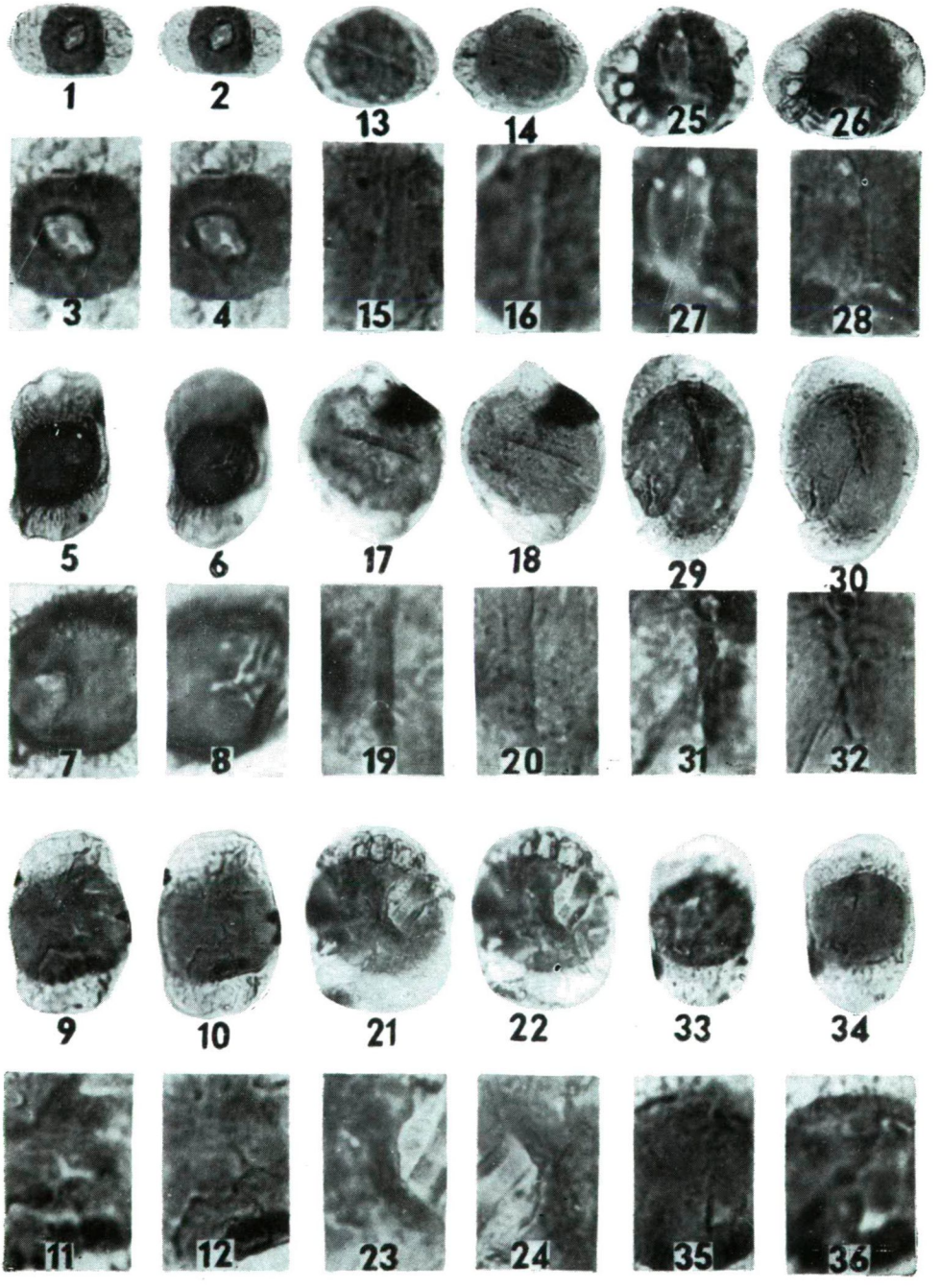
TAGOURDEAU—LANTZ, J. [1962]: Contribution à la connaissance de la microflore du Trias. — Pollen et Spores. *4*. 360.

VENKATACHALA, B. S. and GÓCZÁN, F. [1964]: The Spore—Pollen Flora of the Hungarian „Kössen—Facies". — Acta Geol. Acad. Sci. Hung. *8*. 203—228.

Tafel III

Fig. 1, 2. — *Disaccites* III, So—72—T—1, 11,2/117,1, 500×.
Fig. 3, 4. — *Disaccites* III, So—72—T—1, 11.2/117,1, 1000×.
Fig. 5, 6. — *Disaccites* IV, So—72—T—1, 9,6/117,6, 500×.
Fig. 7, 8. — *Disaccites* IV, So—72—T—1, 9,6/117,6, 1000×.
Fig. 9, 10. — *Limitisporites* fsp.$_2$, So—72—T—3, 8,4/119,2, 500×.
Fig. 11, 12. — *Limitisporites* fsp.$_2$, So—72—T—3, 8,4/119,2, 1000×.
Fig. 13, 14. — *Cf. Striatites* fsp.$_1$, So—72—T—1, 13,1/117,5, 500×.
Fig. 15, 16. — *Cf. Striatites* fsp.$_1$, So—72—T—1, 13,1/117,5, 1000×.
Fig. 17, 18. — *Cf. Striatites* fsp.$_2$, So—72—T—1, 7,4/115,4, 500×.
Fig. 19, 20. — *Cf. Striatites* fsp.$_2$, So—72—T—1, 7,4/115,4, 100×.
Fig. 21, 22. — *Limitisporites* fsp.$_3$, So—72—T—1, 15,2/117,3, 500×.
Fig. 23, 24. — *Limitisporites* fsp.$_3$, So—72—T—1, 15,2/117,3, 1000×.
Fig. 25, 26. — *Cf. Falcisporites* fsp.$_3$, So—72—T—2, 16.2/107,7, 500×.
Fig. 27, 28. — *Cf. Falcisporites* fsp.$_3$, So—72—T—2, 16,2/107,7, 1000×.
Fig. 29, 30. — *Pallidosporites* fsp., So—72—T—3, 10,3/119,3, 500×.
Fig. 31, 32. — *Pallidosporites* fsp., So—72—T—3, 10,3/119,3, 1000×.
Fig. 33, 34. — *Disaccites* V, So—72—T—3, 4,8/101,9, 500×.
Fig. 35, 36. — *Disaccites* V, So—72—T—3, 4,8/101,9, 1000×.

Tafel III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NEW OCCURENCES OF ZEOLITE IN THE MÁTRA MOUNTAINS

by

J. MEZŐSI

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In the upper reaches of brook Madarász, region of Tar, western Mátra Mountains, the so called Lower Andesite Formation of Helvetian age overlying the similarly Helvetian clayey-marly sandstones contain some heulandite associated with few natrolite. Heulandite is found partly in groups of clear crystals grown on the walls of cavities, partly in closely-packed fine-grained crystal aggregates forming rather thin veinlets. The country rock is andesite tuffite.

Clear heulandite also appears in the loose porous andesites of the depth interval 42,0—46,6 m of mapping borehole Hasznos Nr. 1 sunk on the southern slope of Mt. Hegyes, and it is encountered in the outcrop of the andesite, too, where it occurs grown on cavity fillings, accompanied by chlorite and natrolite.

Both occurrences can be regarded as lateral secretion products. The results of their study are completed by chemical analyses, DTA curves and X-ray diffractometric patterns.

In the central Mátra Mountains occurrences of natrolite and chabasite were earlier discovered between the Helvetian sandstones and the Helvetian chloritic-andesite tuffs. Detailed geological mapping led later to the discovery of a new occurrence of zeolite in the western Mátra Mountains.

In the upper reaches of brook Madarász — named „Pena gödör" recently — E of village Tar a formation of interesting habit is exposed. About 100 m W of the junction of the two upper branches of „Pena gödör" greenish-grey clayey tuffites intercalating marly-clayey sandstones (schlier) are exposed which sometimes show yellowish-brown patches due to limonitic stain. At many instances, a gellike, dark-grey to grey colloidal substance filling fissures, cracks or cavities is encountered, on the surface of which there appear minute cracks due to loss of water. This formation of pelitic grain size represents a clay stained by iron hydroxide. In this area cascades 5—6 m deep are sometimes found in the thin-bedded, lamellar sandstones and the tuffites.

The rock seems to be homogeneous by naked eye, but under microscope it consists of pelitic groundmass locally with chloritic embeddings. Sometimes minute andesite lapillis and volcanic sand particles are recognized in it *(Fig. 1)*.

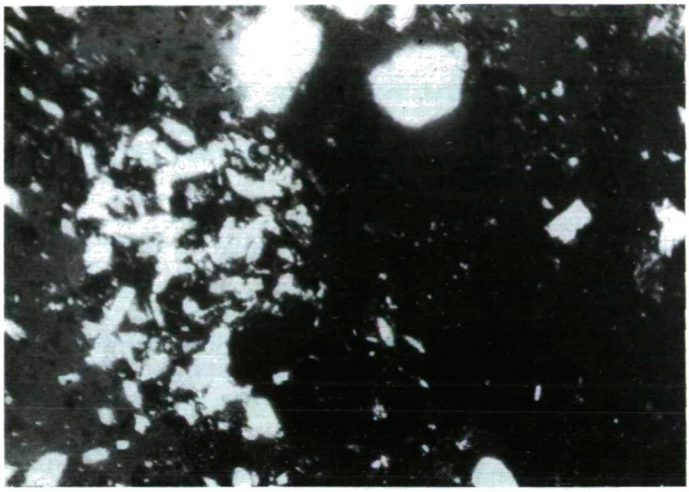

Fig. 1. Fine-grained lapillies in andesite tuffite. Crossed nicols, 40×

In the cement the grain size of the detritus of the rock-forming minerals does not exceed 0,2 mm. Most of these particles is represented by twinned plagioclase feldspar, the minor part by quartz grains which may derive from the underlying marly sandstones or may have been redeposited from a higher level still during diagenesis. No mafic minerals are recognizable in the cement. Chlorite was formed not during the weathering of mafic minerals, but probably during diagenesis. Sometimes, it impregnates the whole rock. It is always granular, radial-fibrous varieties cannot be observed.

The crystals in the detritus of the andesite lapillis hardly attain the size range of 0,1 to 0,2 mm. This detritus, as a rule, does not contain any mafic minerals, any minerals of porphyric segregation. The groundmass is hyalopilitic. It derives from an andesite devoid of mafic minerals or containing but scarce femic components.

This new occurrence is conspicuous for the appearance of zeolite in fissures and sometimes in minor cavities. One type occurs in the cavities of the andesite tuffite *(Fig. 2)*. Clear zeolite crystals of 4—5 mm in size are grown on the walls of cavities. The crystals identified with heulandite are of tabular, lamellar habit *(Fig. 3)*. Their size varies from 1 to 3 mm. On tabular, lamellar crystals the following forms were observed:

001 110 101 $\bar{1}01$

The perfect cleavage along (010) is always distinct. On cleavage face the crystal is commonly of pearly luster. The specific gravity of the clear crystals is 2,17. $n_\beta \sphericalangle c = 23°$. Refraction as determined by immersion method was found to be 1,49, the birefringence as determined by Ehringhaus compensator 0,0056.

The above determinations were confirmed by X-ray diffraction measurements. The results are shown in Table I. These values coincide well with those known from literature. (The X-ray diffraction measurements and their

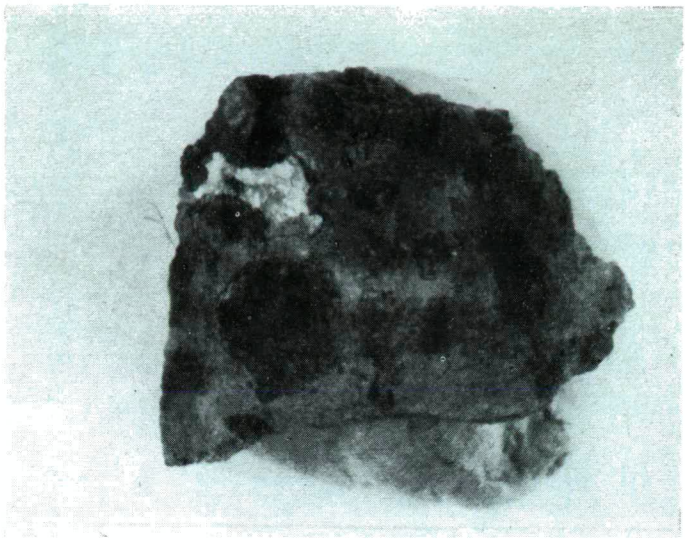

Fig. 2. Heulandite as cavity-filling in andesite tuff. 2× of natural size

interpretation were performed by G. RISCHÁK, research worker of the Hungarian State Geological Institute, whose work is highly appreciated by the author.)

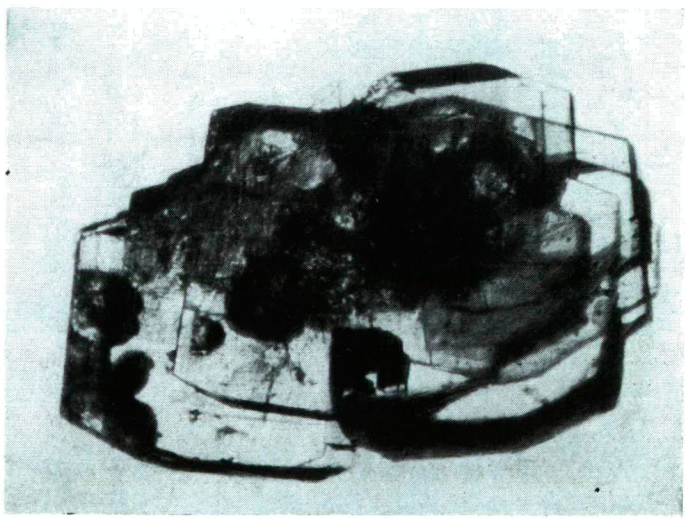

Fig. 3. Crystal of heulandite. 20× of natural size

The other type of zeolite occurs in the fissures of the rock. It fills up thin veinlets within the grey clayey-marly tuffite. *(Fig. 4—5).* These white veinlets form an irregular network throughout the rock mass. Heulandite is represented here by a fine-grained crystalline mass of vitreous or possibly

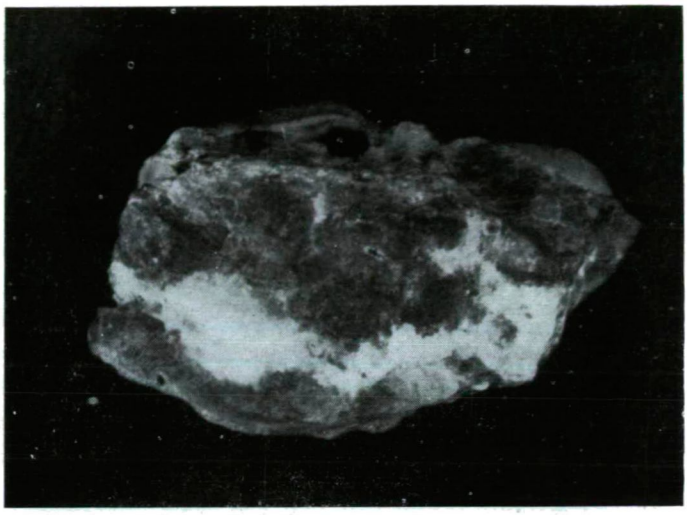

Fig. 4. Crystalline heulandite as fissure-filling. 3× of natural size

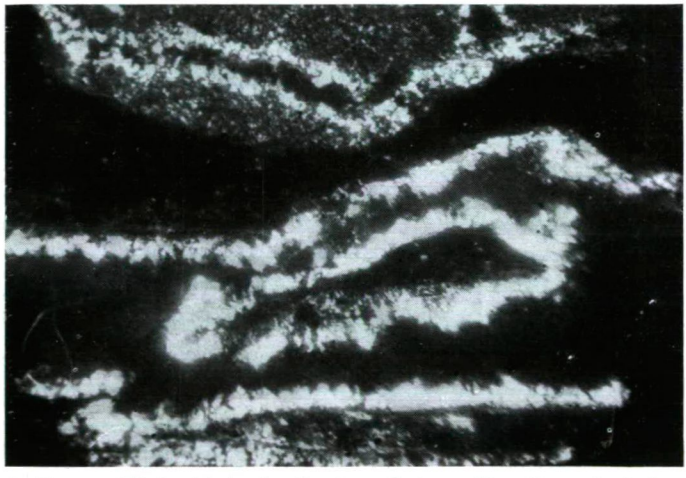

Fig. 5. Fissures filled with heulandite in andesite tuffite. Crossed nicols, 40×

pearly luster. Sometimes calcite accompanied may be observed. The heulandite grains are always smaller than 0,5 mm in size. The microscopic picture of the rock completely corresponds with that of the former type. Zeolite is always of white colour, calcite of yellowish-white. It is peculiar that heulandite sometimes carries very fine needle aggregates, small „brushes" of natrolite. This variety of zeolite is, however, unusually scarce here.

DTA yielded the following results *(Fig. 6.)* After the appearance of a large endothermic peak at about 100 C°, two typical endothermic effects indicative of structural water loss were found at 280 C° and 370 C°, respectively. Koizumi and É. Pécsi–Donáth who studied the behaviour of zeolites including heulandite in dependance on changes in temperature obtained simi-

lar results. The only difference with respect to my results is that I found a small endothermic bend at 280 C° and that I did not find any double peak at 340—360 °C, whereas above 450 °C an endothermic broadening appeared in my experiment, too, just as was the case with that of É. PÉCSI—DONÁTH. It should be noted, however, that quite distinct as they were at about 590°—600° C in É. PÉCSI—DONÁTH's experiment, the effects of endothermic decomposition scarcely discernible in my experiment. The endothermic peaks observed at higher temperatures (670°—910°C) were due to montmorillonitic impurities, for the sample material subjected to DTA was not altogether pure. CAJKOVÁ and HARAMIOVÁ observed an endothermic peak between 160°C and 180°C, an exothermic one at 330°C, and again an endothermic peak at 400°C. The curve obtained by KOSTOV shows endothermic peaks at 170°C and 390°C, and an exothermic one at 330°C.

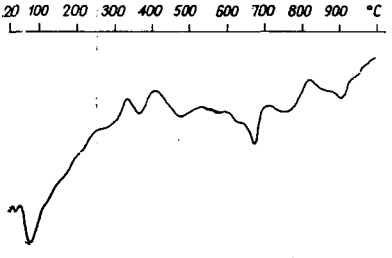

Fig. 6. DTA curve of heulandite

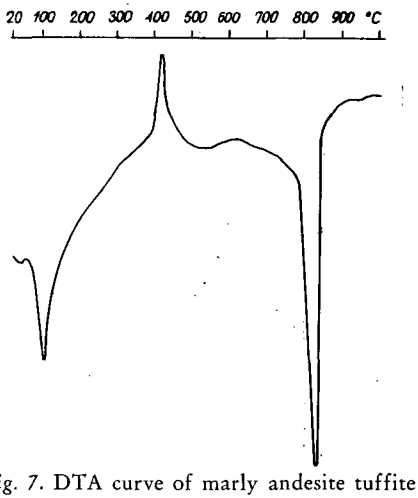

Fig. 7. DTA curve of marly andesite tuffite

Consequently, at low temperatures double peak may appear everywhere, only the temperature values show some shifting following the cases, a fact that may possibly be due to different technologies of sample preparation.

The DTA curve of the grey tuffitic rock in which calcite portions are in most cases visible even to the naked eye has apparently shown the presence of calcite. Beside the endothermic peak due to initial water loss, the DTA curve yielded a large, typical endothermic peak only at 850°C, corresponding to dissociation of $CaCO_3$ *(Fig. 7)*. The exothermic peak at 430°—440°C is due to the presence of finely dispersed marcasite which appears to be responsible for the grey colour, too. The occurrence of marcasite also suggests a reductive environment rather than an oxidative one, since otherwise the appearance of marcasite, i. e. the presence of ferrous iron could not be accounted for.

The habit shown by the heulandite found in borehole Hasznos Nr. 1 sunk on the southern slope of Mt. Hegyes (529,2 m) was similar to that of the crystallized heulandite. The boring started from the Helvetian dacite tuff near to the rim of the Tortonian andesite of the Mount Hegyes. At 39 m depth

the dacite tuff showed a sharp delimitation from the Helvetian andesites belonging to the Lower Andesite Formation. This rock is brownish grey, slinghtly altered, porous, extending to 46,6 m depth, from where downwards we find agglomeratic andesite tuffs to 51 m depth, where the former rock is underlain by fresh, dark-grey andesites 2 m thick which may represent a small apophyse of the Tortonian andesites of Mt. Hegyes. The andesites within the range of 39,0—46,6 m are rather homogeneous, loosely crumbling, with cavities in which ferric hydroxide segregations can often be recognized. The feldspar particles 2,5 to 3 mm in size are well differenciated from the ground mass. No dark rock-forming constituents are visible to the naked eye; even when viewed with a microscope, the rock exhibits only traces of femic components which must have been rather scant at the very beginning.

In depth interval from 42,40 to 46,60 m the rock mass is traversed by yellowish-white calcite veinlets 1—3 cm thick. Sometimes bluish-grey veinlets of chalcedony a few mm thick are observed. This occurrence is conspicous for the fact that groups of clear heulandite crystalgroups 2—4 mm across appear in the cavities of the rock *(Fig. 8)*. The core is ochre having the appearance

Fig. 8. Crystal group of heulandite in porous pyroxene-andesite. Crossed nicols, 40×

as if it were impregnated by zeolite. The crystals exhibit the same physical properties as do the crystallized specimens found in „Pena gödör". The X-ray diffraction data also correspond to those obtained for the crystallized material of „Pena gödör". The values are given in Table I.

An outcrop of this brownish-grey, porous rock appears to be the andesite mass at the northern side of the road Pásztó—Mátrakeresztes extending on the southern slope of Mt. Hegyes. This rock is also porous, sometimes containing oxidized portions distributed irregularly. The upper part is represented by lava agglomerates, the lower one has a tuffaceous habit. In the lava rock the porphyric segregates are also well differentiated from the ground mass. The columnar feldspars 1—4 mm across belong to the labradorite series. Of the rather poor pyroxenes, augite is most abundant, hypersthene being scarcer. Consequently, the rock under consideration is a pyroxenic andesite.

Here also, we can find heulandite in the cavities of the rock *(Fig. 9)*. It is represented, here too, by groups of clear cristals of vitreous luster. In some cavities heulandite is found overgrown by natrolite. The genetic succession of the minerals is as follows. Earliest of all appears chlorite on the wall of the cavities. It is overgrown by heulandite on which natrolite, the youngest mineral, is accumulated.

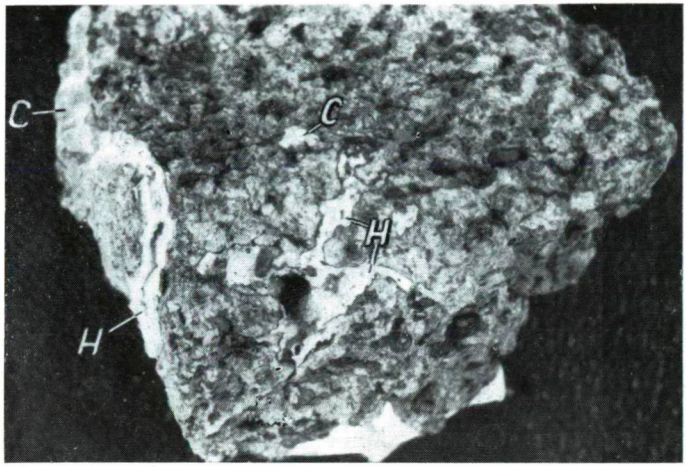

Fig. 9. Heulandite in the cavity of porous pyroxene-andesite. $^1/_2$ natural size
C=calcite, H=heulandite

The X-ray diffractometric measurements were performed by using a Mueller Mikro 111 diffractometer. CuKα served as source of radiation. Heulandite is not too frequent in the geological formations of Hungary. The best occurrence is at Nadap (Velence Mountains). Over there it was discovered in a few cm thickness at the granite-andesite contact. It can be regarded as a remobilized mineral produced by lateral secretion (KOCH). The heulandite of Füzérkomlós occurs in the cavities, fissures of pseudoagglomerated hypersthene-augitic andesites being represented by 0,5 cm crystals in assemblage of chalcedony, tridymite, opal, calcite, aragonite, chabasite and barite.

The heulandite crystals up to 2 cm across occurring at Sátoros are associated with chabasite, desmine, and laumontite.

In addition, heulandite has been recorded from the hill „Sulyom tető" in the valley of river Zagyva.

When considering the new occurrence in the Mátra Mountains including that of „Sulyom tető" at Nagybátony, we can realize that these are all within the Lower Andesite Formation overlying the Helvetian clayey-marly sandstones. So their distribution and changes in dependence of the height above sea level must be ascribed to later crustal movements.

Since in these places we can hardly encounter effects of hydrothermal solutions, it is merely the agents expounded by E. SZÁDECZKY-KARDOSS that may have been involved in the formation of zeolites.

Accordingly, one of the prerequisites of zeolite formation is the abundance of volatiles in the source material. Typical representatives of this facies may

presumably develop only at relatively high pH in an alkaline environment, chiefly in volcanic areas or in their neighbourhood, due to magmatic mobilization. If a high-temperature lava or pyroclastic material superimposes a volatile-rich sedimentary rock — clayey-marly sandstone, in the given case — or eventually is introduced into a shallow sea, then water vapour will develop penetrating the lava or eventually tuffite whose abundance in volatiles will thus increase. Here it is not the temperature gradient, but the pressure gradient that is of decisive importance. Any mobilized element migrates from an environment of higher pressure to another of lower pressure, regardless of whether this is opposed to the temperature gradient or not. Like in the case of the zeolites along the northern shore of Lake Balaton, the zeolites of the Mátra Mountains were not produced by any ascendent hydrothermal solution, but came about under the effect of water vapour released by glowing pyroclastics ejected during volcanic activity, due to the mobilization of elements provoked thereby. Zeolites of such genesis formed first of all at the contact between the clayey-marly sandstones and the Lower Andesite Formation. This is the reason why in the Mátra Mountains and surroundings zeolite is known to occur only in places like this. In the genesis of the zeolites occurring in the mine of Gyöngyösoroszi the hydrothermal solutions may also have been largely involved.

As well-known, the formation of zeolites commonly requires a high pH. The presence of this latter is substantiated by the fact that calcite as an associated mineral is always present, whether the occurrence in „Pena gödör" or the stratigraphic column of mapping borehole Hasznos Nr. 1 on Mt. Hegyes is considered.

Here and there heulandite is encountered in a chloritic environment. In such places a definite order of segregation can be observed. The oldest mineral in the cavities is chlorite which is followed by heulandite, the youngest segregate being natrolite. If we consider the formation temperature of these minerals, we shall realize that it also is roughly in line with the aforementioned order, since chlorites can be formed between 100° and 300°C, zeolites between 70°—90°, and calcite above 100°C. It thus stands to reason that these minerals follow each other in the order determined by the temperature.

Earlier it was pointed out by E. Szádeczky-Kardoss that the genetic succession of the minerals is partly controlled, or at least largely influenced, by geoenergetic factors dependent on lattice, characteristics (ionic potential, compound potential). Accordingly, first the cubic, then the foliaceous and finally the fibrous zeolites are formed. Considering the values of the ionic potential, the following data were obtained for the minerals occuring here:

compound potential of pennine $(Mg,Al)_3(OH)_2AlSi_3O_{10}=2{,}02$
compound potential of heulandite $CaAl_2Si_7O_{18}\cdot 6\ H_2O=0{,}88$
compound potential of natrolite $Na_2(Al_2Si_3O_{10})\cdot 2\ H_2O=0{,}83$

In the case of zeolites the number of the water molecules is not taken into consideration.

In conclusion, these zeolites can also be taken for lateral secretion products in the formation of which the volatiles were largely involved.

TABLE I

2Θ values of diffraction patterns of heulandite crystals from „Pena gödör" and Hasznos boring No. 1. comparing to those of the heulandite from locality Zakyl. Radiation CuKα.

„Pena gödör" crystalline	*„Pena gödör"* grained	Hasznos boring No. 1.	*Zakyl*
2Θ	2Θ	2Θ	2Θ
10,00	9,98	10,00	10,10
		11,40	11,18
			11,91
			13,30
			15.42
			16,64
17,50			17,77
			8,85
			19,39
			20,75
			21,74
22,50	22,50	22,45	22,55
	22,85	22,80	
			25,62
		26,05	
26,49			26,43
			27,38
27,98	27,90		
28,20	28,20	28,25	
28,70	28,60	28,60	28,86
30,20	30,00	30,05	
			30,67
			31,34
32,20	32,02		32,20
32,98	32,90	32,90	
			33,15
35,80	35,55	35,60	
37,02		37,01	
		46,40	
51,02	51,00	50,90	

REFERENCES

Cajková, M.—Haramiová, S. [1959]: Niektové vyskyty zeolitov v dutinách andezitov na Slovensku.—Geol. práce. Zosit *54*. Bratislava. pp. 191—224.

Doelter, C. [1921]: Handbuch de Mineralchemie. *Band II.* Verlag von Theodor Steinkopff, Dresden.

Koizumi, M. [1953]: Water in minerals I. The differential thermal analysis curves and the dehydration curves of zeolite—Min. Journal I. pp. 36—47.

Koizumi, M. and Kiryama [1954]: Thermal and X—ray studies on stilbites and heulandites. =Kobutsugaku Jasshi I. pp. 334—343,

Koch S.: Magyarország ásványai. In print.

Костов, И. [1957]: Минерология. София. Държавно издателство «Наука и изкуство»

Mezősi, J. [1961]: Zeolite occurrence in the Mátra Mountain.—Acta Miner. Petr. *XIV.* pp. 67—74.

Mezősi J.: Az I.—34—4—B—a—3 számú földtani térkép magyarázója. In print.

Pécsi—Donáth, É. [1963]: A zeolitok termikus bomlásának vizsgálata DTA módszerrel. — Földtani Közlöny *XCIII.* Agyagásvány füzet pp. 25—31.

Strunz, H. [1957]: Minerologische Tabellen. Leipzig. Akademische Verlagsgesellschaft.

Szádeczky-Kardoss, E.—Erdélyi, J. [1957]: A balatonvidéki bazaltok zeolitjainak képződéséről. — Földtani Közlöny *LXXXVII.* pp. 302—308.
Szádeczky-Kardoss, E. [1958]: On a ptc rock system.—Geokémiai Konferencia. Manuscript.
Szádeczky-Kardoss, E. [1958]: Magma, volatiles and the crust of the Earth.—Geokémiai Konferencia. Manuscript.
Szádeczky-Kardoss, E. [1964]: A kőzetek teljes rendszerezése. — Kárpát-balkán asszociáció Konferencia. Balatonfüred. Manuscript.
Tröger, W. E. [1952]: Tabellen zur optischen Bestimmung der gesteinsbildenden Minerale. Stuttgart. E. Schweizerbart'sche Verlagsbuchhandlung.

CHANGES IN AREA AND DIRECTIONS OF STREAM EROSION IN THE EASTERN PART OF THE HUNGARIAN BASIN (GREAT PLAIN) DURING THE PLIOCENE AND PLEISTOCENE

by

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The last marine sediments of the Hungarian Basin (Great Plain) were deposited in the Lower Pliocene in brackish water of the Pannonian sea. Thereafter, in the Upper Pliocene (Levantian), the Great Plain become a fluvio-lacustric area. The sediments produced in the Upper Pliocene do not cover the territory of the basin, uniformly as subsequent Pleistocene and Holocene alluvial deposits form here and there a direct cover of Pannonian marine sediments, and Upper Pliocene sediments are absent. The upper limit of the Pannonian strata is at various structural depths within the basin. The differences were caused by later movements of the Earth's crust resulting in further differences in the development of regional units. [JASKÓ 1947, KERTAI 1957, KŐRÖSSY 1956, 1957, 1963, ERDÉLYI 1960, CSIKY 1963, RÓNAI 1964].

The eastern part of the Hungarian Basin (Tiszántúl) was filled up by rivers running from the borders: the Zagyva from NW, the Sajó and the Hernád from North, the Bódva and the Tisza from NE, the Szamos, the Körös and the Maros from East, as well as by their predecessors.

We have data on the historical development of the river system of Tiszántúl in plenty. [SÜMEGHY 1944, ERDÉLYI 1960, SOMOGYI 1961, BULLA 1962, URBANCSEK 1960, 1962.] Yet the heavy-mineral composition of the Pliocene and Pleistocene sandy sediments have not been analyzed so far although a knowledge of the composition of recent alluvia and their comparison with the former might help in drawing up a correct picture of the palaeohydrographic evolution.

Therefore, similarly to earlier examinations the heavy-mineral composition of further borings has been analyzed. *Figure 1* shows the location of the evaluated borings grouped in profiles.

Profile I *(Figure 2)* contains the borings of Szolnok and Törökszentmiklós. The heavy-mineral composition of the boring of Szolnok is characterized by a lower percentage of hypersthenes (1,7 to 1,9%) and by a higher

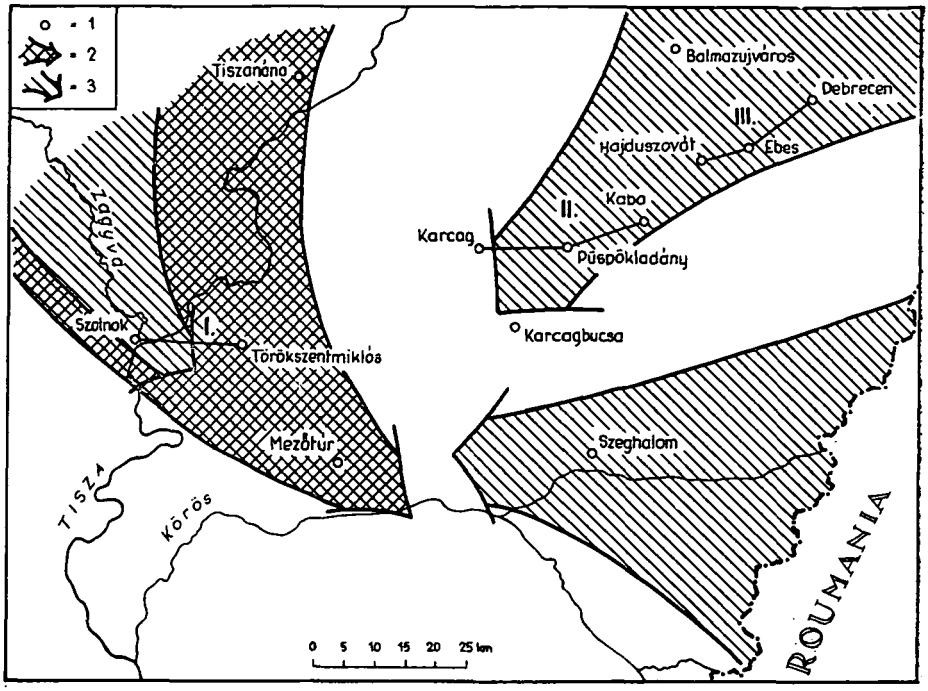

Figure 1. General plan of borings and profiles elaborated so far
1. Situation of the borings
2. Stream-erosion direction of the Palaeo-Zagyva
3. Stream-erosion directions of the sediments whose the composition is similar to that of alluvia of present-day rivers.

amount of garnet (15 to 39%), (See *Figure 2* and Table). By these of his properties it is similar to the alluvia of present Zagyva river, which means that the stream erosion has taken place, also in this case, from the NW *(Figure 1)* [MOLNÁR, 1964]. Sediments of similar composition are known from the borings of Pély and Kisköre, situated to the North of this area. [MOLNÁR 1964]. The composition of samples taken at the greatest depth in the Szolnok boring (309 m) differ from the overlying strata by the absence of hypersthene and brown amphibole, by having a smaller amount of garnet (8;8%) and by a higher percentage of calcite-dolomite (20%). This sediment did not come from the same area as the present alluvia of the Zagyva.

The other boring on Profile I called Törökszentmiklós is situated at 20 km to the Eeast of Szolnok *(Figure 1)*. The high amounts of hypersthene (6 to 28%), augite (3 to 9%) and brown amphibole (5,2 to 9,6%) in the material prove that erosion was coming from the E or NE. *I.e.* the alluvia of the Körös and those of the rivers to the NE contain considerable amounts of the above mentioned minerals [MOLNÁR 1964].

Figure 3 shows heavy minerals in samples taken at 25 to 31 metres in the boring of Törökszentmiklós. The light-coloured minerals are, for the most part hypersthenes and augites. The opaque inclusions of hypersthenes as well

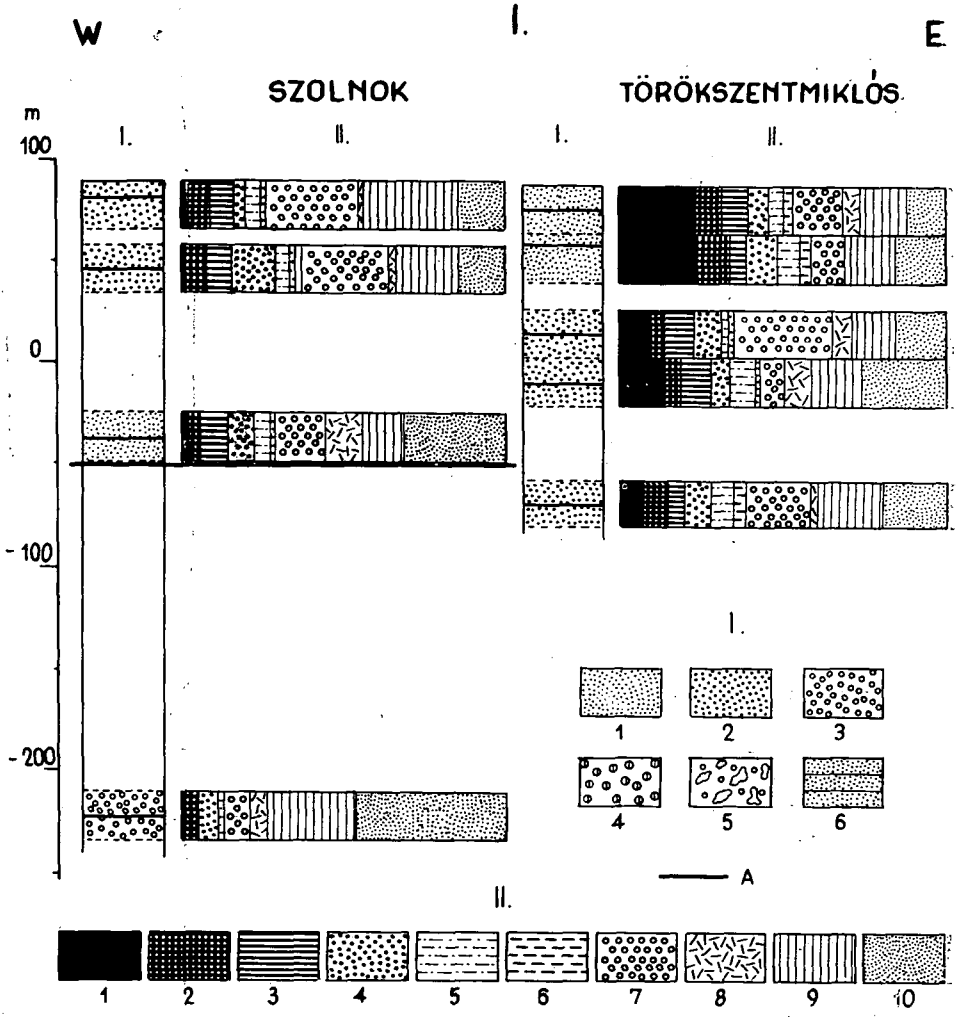

Figure 2 (Profile I)

I. Granulometric composition:

1. Fine sand (0,06 to 0,1 mm)
2. Fine-grain sand (0,1 to 0,2 mm)
3. Medium-grain sand (0,2 to 0,5 mm)
4. Coarse-grain sand (0,5 to 2,0 mm)
5. Gravel
6. Sandstone

II. Heavy-mineral composition:

1. Hypersthene
2. Augite
3. Brown amphibole
4. Magnetite
5. Chlorite
6. Bluish-green amphibole (hornblende)
7. Garnet
8. Limonite
9. Other minerals (total)
10. Weathered mineral

A.: Lower limit of the sediments of the Tisza catchment area.

Mineral composition of the samples investigated

Serial number	Boring		Dominantly magmatie minerals										Dominantly metamorphic minerals												Other minerals						Total quantity of the heavy-minerals in the examined fraction	Diameter of examined fraction in mm	Dominant grain diameter in mm
	LOCALITY	DEPTH m	Hypersthene	Other rhombic pyroxenes	Augite	Diopside	Brown amphibole	Magnetite	Ilmenite	Biotite	Apatite	Titanite	Zircon	Chlorite	Tourmaline	Epidote	Zoisite	Rutile	Bluish green amphibole	Actinolite — tremolite	Anthophyllite	Garnet	Staurolite	Cyanite	Andalusite	Glaucophane	Serpentine	Calcite-dolomite	Glauconite	Pyrite	Limonite	Other micas	Weathered minerals			
1	Szolnok	2,8—9,5	1,9	2,5	6,2	4,9	7,5	3,7			6,2		0,6	4,4	4,4	3,7	0,6	1,2	1,2	3,2		28,9	0,6	0,6	0,6			1,2		0,6	1,9	4	14,4	3,1	0,1—0,125	0,1—0,2
2	Szolnok	41—46	1,3	6,0	4,7	7,7	1,3	6,0			3,3			4,0	2,0	1,3	0,7	1,3	1,3	0,7		39,3	0,7	2,7						0,7	2,7	0,7	14,6	2,7	0,1—0,125	0,1—0,2
3	Szolnok	125—130	1,7		3,7	2.2	3,7	13,0			4,4		0,5	4,9	0,5	1,1			1,7	1,1		15,7	0,5	0,5						0,5	11,3	1,1	31,9	0,8	0,1—0,125	0,05—0,1
4	Szolnok	309—317			4,3	1,3		6,8			0,6			1,3		1,3			0,6	0,6		8,8		0,6	0,6			20,8			4,7	1,3	46,4	11,0	0,1—0,2	0,2—0,5
5	Törökszentmiklós	12—13	22,8	0,5	8,4	0,5	9,6	7,3		1,1	1,7			3,9	2,2	0,5	1,0	1,1	2,8			15,8			0,5						5,1	2,8	12,4	1,9	0,1—0,125	0,1
6	Törökszentmiklós	25—31	23,8	0,5	9,3	1,5	5,7	9,3		1,0	2,1			7,7	1,5			0,5	3,1	2,1		10,3	1,5	0,5							1,5	2,6	15,5	1,5	0,1—0,2	0,1
7	Törökszentmiklós	72—77	9,0	1,7	3,4	1,1	9,6	6,2			4,0			2,8	1,7	0,6		0,6	1,7	1,1		31,1	2,2	0,6				0,6			6,2	0,6	15,2	1,5	0,1—0,2	0,1—0,2
8	Törökszentmiklós	97—99	12,9		4,8	1,1	9,6	5,9		2,7	0,5			7,6	1,1				1,6	3,2		8,1	1,1	0,5				1,1		1,1	6,5	4,8	25,8	1,4	0,1—0,2	0,1—0,2
9	Törökszentmiklós	145—161	6,6	0,9	7,5	0,9	5,2	7,9		0,9	4,3	0,4		7,0	4,7	0,9	0,9	0,4	3,8	2,9		20,1	0,4	1,4						0,4	1,9	0,9	19,7	1,4	0,1—0,125	0,1—0,2
10	Karcag	24—29	21,9	0,6	10,4	1,2	9,8	7,5			0,6			2,9	1,7			0,6	1,7	1,2		12,2	0,6							2,3	6,3		18,5	2,1	0,1—0,2	0,1—0,2
11	Karcag	78—83	9,7		8,1	1,6	4,8	16,1			1,6			21,1	0,5	1,1			1,1			5,4						0,5		1,6	3,2	2,7	19,9	1,9	0,1—0,2	0,1—0,2
12	Karcag	121—124	6,5	1,8	7,7	1,2	9,5	8,9		1,2	2,4			7,1	1,2				3,5	1,2		10,0	0,6	0,6						3,5	4,1	0,6	28,4	1,9	0,1—0,2	0,2—0,5
13	Püspökladány	50—59	11,3	0,5	9,1	1,6	4,8	9,1		4,8	0,5			15,0	1,0	0,5	0,5		0,5	1,0		2,7									3,2	4,8	29,1	2,8	0,1—0,2	0,1—0,2
14	Püspökladány	126—130	16,0		13,5	0,6	9,3	8,0		0,6	1,3			3,7	0,6	0,6			6,2	0,6		11,1	0,6							1,9	1,9	1,3	22,2	5,9	0,1—0,2	0,3—0,5
15	Püspökladány	275—280	6,6	0,5	13,2		11,5	4,9		4,4	1,1			7,7	1,1				2,8	1,6		12,0	0,5							0,5	1,6	1,1	28,9	3,3	0,1—0,2	0,2—0,4
16	Püspökladány	310—315	1,8		5,8		22,7	8,1		1,1	0,6			6,9	0,6				4,7	0,6		20,9						0,6	4,7		3,4		17,5	6,7	0,1—0,2	0,4—0,5
17	Püspökladány	420—425	2,2		2,2		4,4	15,3		0,7				2,2	0,7			0,7		0,7		7,3				0,7				2,2	3,7	2,2	54,8	2,5	0,1—0,2	0,4—0,5
18	Püspökladány	528—531					2,4	20,0						3,7	0,6			1,2	0,6	0,6		23,0	1,2			0,6				0,6	7,9		37,6	2,9	0,1—0,2	0,5—1,0
19	Püspökladány	635—640				0,6	4,1	12,5						2,4	0,6	0,6			1,2			20,8	1,2					0,6		2,4	3,6	0,6	48,8	8,6	0,1—0,2	0,5—1,0
20	Kaba	54—58	11,3	1,0	15,1	1,0	13,5	10,7			1,0			2,1	1,0		0,5	1,6	4,3	1,0		14,6		0,5						1,0	5,7		14,1	2,3	0,1—0,125	0,1—0,2
21	Kaba	124—137	13,8	1,8	18,3	0,6	6,9	10,1		0,6	0,6			5,1	1,2				2,6	0,6		7,6									5,1	1,8	23,3	4,1	0,1—0,125	0,4—0,5
22	Kaba	209—211	23,5	1,5	21,9		2,3	12,4						2,3								10,6										4,6	21,9	11,6	0,1—0,25	0,5—0,7
23	Kaba	216—225	5,1		3,9	1,3	15,4	10,9						1,9	0,6	1,3			1,9	1,3		27,6								3,2	4,5	0,6	20,5	2,9	0,1—0,2	0,5
24	Hajduszovát—1	886—892					3,6	6,4		50,7				8,6														0,7			7,1		22,9	0,8	0,1—0,2	0,05—0,1
25	Hajduszovát—1	1060—1066								0,7				37,6								1,3						0,7			4,0	7,4	48,3	0,9	0,1—0,125	0,05—0,1
26	Hajduszovát—1	1150—1156								0,8				29,8								0,8										11,9	56,7	0,9	0,1—0,125	0,1—0,2
27	Hajduszovát—1	1324—1334								1,8				20,2								0,9									2,8	2,8	71,5	1,2	0,1—0,2	0,1—0,2
28	Ebes—3	817—822		0,9			0,9	4,3			1,7			62,0	2,6							6,0									4,3	0,9	16,4	0,8	0,1—0,125	0,1—0,2
29	Ebes—3	957—962						1,8			0,9			73,2	0,9							1,8						0,9				0,9	19,6	0,8	0,1—0,2	0,1—0,2
30	Ebes—3	1500—1504		0,6	2,2			2,2			1,1			28,8	0,6			0,6				19,9						0,6		21,5	3,2	1,2	14,3	0,9	0,1—0,2	0,05—0,1
31	Debrecen—4	1,3—	24,6		11,6	4,1	3,0	7,6			1,0			5,6	2,1	1,5		0,5	2,1			13,6			0,5			0,5			6,1		15,6	3,1	0,1—0,125	0,2—0,3
32	Debrecen—4	28,4	21,9	6,1	12,2		7,9	9,7			1,8		0,6	2,4	0,6	1,3			3,7			12,2		1,3				1,3			6,1		10,9	2,3	0,1—0,125	0,2—0,4
33	Debrecen (Klinika)	33,5—37,0	25,4		21,2	1,2	5,5	7,3		1,1				0,6	1,6			0,6	2,8	1,6		12,4	0,6	0,6	0,6						1,1		15,8	2,2	0,1—0,2	0,2—0,5
34	Debrecen—4	50,3	5,3	3,1	7,9		11,6	12,1			2,1			3,6	3,1			0,5	2,1	1,1		22,1	0,5	1,1				1,1			5,3		17,4	1,4	0,1—0,125	0,1—0,2
35	Debrecen (Klinika)	99 —105	28,4		14,2		10,9	8,4						2,6		0,7			4,5	1,3		9,0											20,0	9,2	0,1—0,2	0,5—2,0
36	Debrecen (Klinika)	116 —127	14,2	1,3	10,0	0,4	12,9	4.2			2,2			3,1	0,8	0,4		0,4	7,1			12,9			0,4					9,4	1,7		18,6	3,9	0,1—0,2	0,5—0,1
37	Debrecen (Klinika)	127 —139	12,5		9,8		4,9	7,1			0,6			4,9	0,6							4,9		0,6				0,6		19,1	3,8	1,1	29,5	6,0	0,1—0,25	2,0—5,0
38	Mezőtúr	7—9	5,7		7,9	1,1	25,5	6,8		0,6	1,1	1,1		12,4	1,1			0,6	5,1	2,2	0,6	3,4		1,1							2,8	1,1	19,8	0,5	0,1—0,125	0,05—0,1
39	Mezőtúr	51—57	15,8	1,4	11,5	1,4	4,3	9,3			0,7			7,1	2,1			0,7	2,1			13,6		1,4							5,0	4,3	19,3	1,6	0,1—0,2	0,1—0,2
40	Mezőtúr	94—101	9,7	0,5	9,7	0,5	12,7	7,1	0,5		1,5			10,2	0,5	1,5			2,0	1,0		17,8		0,5		0,5		0,5			5,1	1,0	17,2	1,3	0,1—0,2	0,1—0,2
41	Mezőtúr	216—219	11,2	0,5	3,7	0,5	9,1	10,6	0,5		2,7	0,5		2,7	2,7	0,5	0,5	0,5	3,7	1,6		20,8									4,8	0,5	22,4	2,2	0,1—0,2	0,1—0,2
42	Mezőtúr	401—406	1,2	2,3	4,1		4,1	10,5			1,2			9,3	0,6	1,8		0,6	2,3	0,6	1,2	4,6	1,2	1,2				2,9			5,3		45,0	4,5	0,1—0,2	0,2—0,5
43	Mezőtúr	484—488			0,7	0,7		17,9			1,4			3,6	0,7			0,7	0,7	0,7		8,7									15,9		48,3	1,2	0,1—0,125	0,05—0,1
44	Mezőtúr	594—597		2,9	6,4	2,9	1,8	15,2			1,2			4,0	0,6	1,8			1,8	0,6		21,0	1,2	1,8						3,5	3,5	0,6	29,2	4,0	0,1—0,2	0,2—0,4
45	Mezőtúr	616—622		0,6	1,2	2,5	1,9	20,8			0,6			4,4	1,9	3,2	0,6			0,6		13,8	1,9					1,2		7,6	10,1		27,1	1,3	0,1—0,2	0,1—0,2
46	Szeghalom	5—8	7,5	1,5	9,5	2,0	17,5	6,0		1,0	1,5			9,0	1,0	0,5			2,0	0,5		6,5			0,5						1,5	0,5	31,5	3,8	0,1—0,2	0,1—0,2
47	Szeghalom	43,5—49	17,0	1,7	17,0	1,1	19,3	0,6	0,6	1,7	3,4	0,6		4,6	0,6	1,7			5,6	2,3		7,4		0,6							1,7	0,6	11,9	7,9	0,1—0,2	0,2—0,5
48	Szeghalom	230—235	2,9	0,5	4,9	0,5	8,5	8,5		1,0	2,9			8,9	1,9	0,5		0,5	1,9	0,5		14,4	1,0	1,0		0,5				8,5			30,7	2,3	0,1—0,2	0,2—0,3
49	Szeghalom	310—315	0.6	2,9	5,4	1,2	5,9	16,0	0,6		1,2			15,5	1,8				5,4	1,2		3,6						0,6			3,6	3,6	30,9	2,7	0,1—0,2	0,2—0,3
50	Szeghalom	349—357	4,7	0,4	6,2		14,1	7,9	0,9		0,9			15,1	0,9				3,8	1,5		7,9									2,9	0,9	31,9	3,0	0,1—0,2	0,2—0,3
51	Szeghalom	393—398	9,7	0,5	11,7	1,5	13,1	5,8		0,5	2,4			2,9	1,5				0,9	0,9		15,0	0,5	0,5							8,3		24,3	3,4	0,1—0,2	0,2—0,5
52	Tiszanána	50—58	1,7		3,3	0,6	7,2	2,8		1,7	3,9			1,7	4,5	0,6			1,2	1,2		50,6		0,6				1,7			5,0		11,7	1,2	0,1—0,125	0,05—0,1
53	Tiszanána	148—150	3,3	2,8	2,8	1,9	3,8	3,6			3,3	0,4		1,4	4,2			2,3	0,9	0,4		32,3	0,9	0,5						0,9	6,1		18,2	0,9	0,1—0,125	0,05—0,1
54	Balmazújváros—2	860—866			0,8			0,8			0,8			38,4				0,8				0,8			0,8						9,2	2,5	45,1	0,8	0,1—0,125	0,05—0,1
55	Karcagbucsa—2	1364—1369						1,5			1,4			10,1	2,9							20,3									15,5	1,4	36,9	0,8	0,1—0,2	0,2—0,4
56	Karcagbucsa—2	1386—1391		0,6			0,6	1,7		3,5	1,1		0,6	30,5	5,7							12,6									8,0	2,9	32,2	1,1	0,1—0,2	0,1—0,2
57	Karcagbucsa—2	1500—1504												86,2		0,6						2,5					3,8				1,9		5,0	1,5	0,1—0,1	0,1—0,2

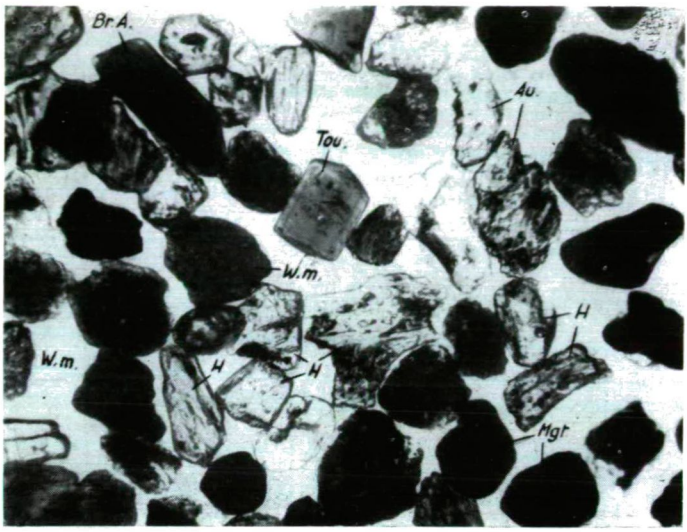

Figure 3 Heavy minerals sampled at 25 to 21 m, in the Törökszentmiklós boring (|| nicols, in nitrobenzene, fraction of 0,1 to 0,2 mm ∅). Magnification: 80—100×.

as their fringed ends are clearly seen. The columnar, somewhat darker mineral with clearer borders, on the left side of the figure, represent brown amphibole, the idiomorphic mineral in the centre is tourmaline.

The differences in the heavy-mineral composition of the materials sampled at the same depths in both of the borings, as well as the similarity of composition in the alluvia of present rivers proves that a river coming from the NW deposited its alluvia in the Szolnok area, whereas at Törökszentmiklós the deposits were transported by a river coming from the E or the NE, and filled up this part of the basin.

Sediments examined earlier and sampled at greater depths in the borings of Pély, Kisköre, to the North, as well as those situated to the South, at Gyoma and Szolnok, have shown that the river coming from the NW or the North, deposited older sediments as far as Gyoma, *i.e.* to the East and the South far beyond the present alluvial area *(Figure 1)*. This finding is in accordance with the courses of the Upper Pliocene Palaeo-Zagyva and Palaeo-Sajó-Hernád drawn up by Sümeghy [1955]. Urbancsek [1962] traced on this territory, the limits of the area of high-ferruginous artesian waters, which is in fairly good compliance with the deposition area of the original rivers above mentioned. The higher iron content of these sediments may be in connection, in addition to the aggressivity of water, with the larger amount of magnetite and limonite. Kriván and Mrs. Nagy, relying upon a palynological analysis of the material transported by the rivers, have proved that an erosion coming from the NW, originates in the Pannonian beds on the border of the Mátra Mountains, and had taken place in the Upper Pleistocene [Kriván—Mrs. Nagy 1963].

Fine or fine-grain sand has been sampled in the upper horizons of borings from Szolnok and Törökszentmiklós *(Figure 2)*. In the lowermost horizon of

the Szolnok boring, medium-grain *i.e.* coarser sand has been found as well; another expression of the differences between the depositions (erosion) of the lower and upper levels.

Profile N°. II *(Figure 4)* touches Karcag, Püspökladány and Kaba to the East of the former. The composition of the Kaba boring is characterized by hypersthene and augite playing an important role, together yet decreasing downwards (see Table). As it is known today the two characteristic minerals

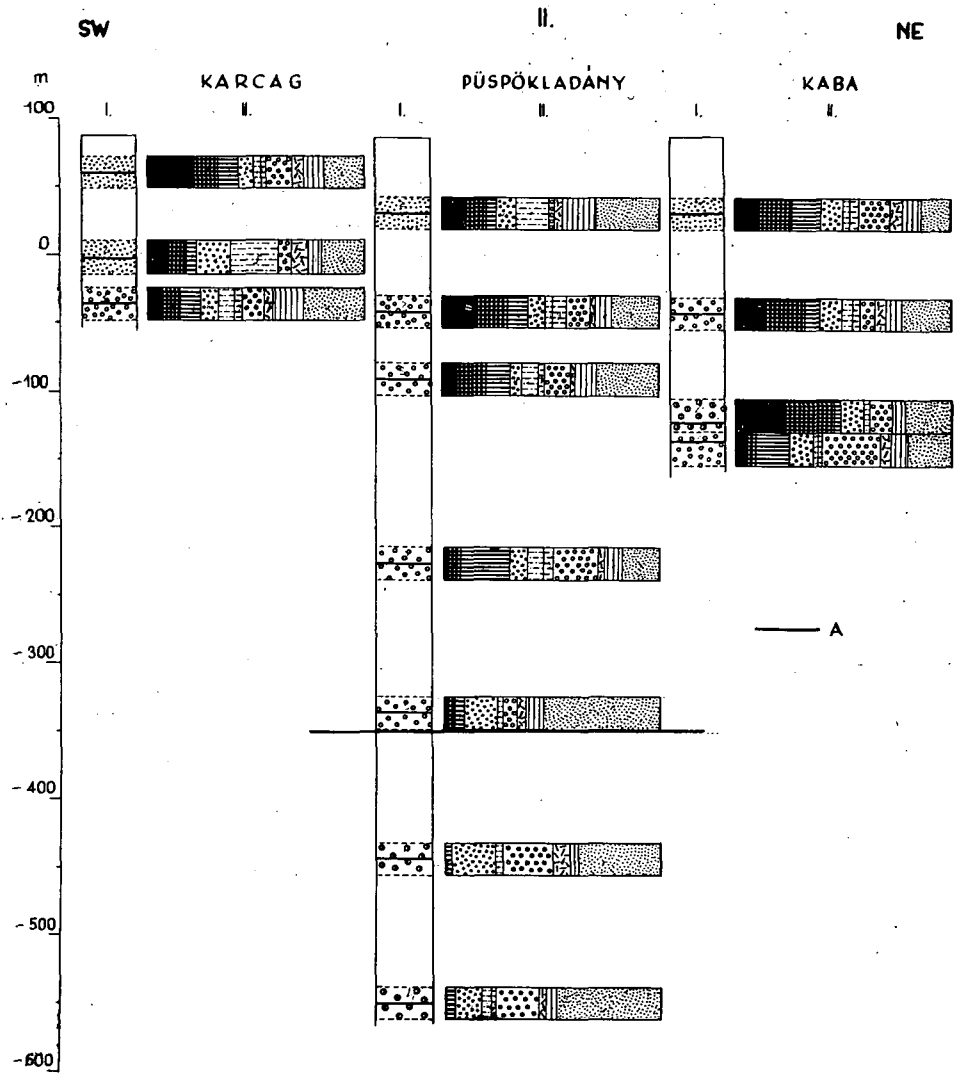

Figure 4 (Profile II). (For legends to granulometric and heavy-mineral composition see Figure 2)
A.: Lower limit of the sediments of the Tisza catchment area.

of the northern affluents of the Tisza and, to the NW of the Tisza, itself, are hypersthene and augite. In the alluvia of the Körös and the Maros coming from the East brown amphibole is also considerable. The sediment examined in the Karcag boring must have been transported to this place, from the NW, by the Palaeo-Tisza-Szamos as suggested by BULLA [1962]. The same holds true for the materials from the Püspökladány boring, with the difference that, at this place, the amount of brown amphibole is more increasing, while that of hypersthene and augite keeps decreasing probably upon the influence of the Körös.

The sample taken at a depth of 420 to 425 m represents a transition to the underlying sediments: below the sediments of the Tisza-river-system, sediments of a heavy-mineral composition differing from that of present alluvia have been found. The lower deposits are characterized by a small amount of brown amphibole and high magnetite and garnet content as well as by a large amount of weathered minerals (37 to 54%). Further data are needed to determine the direction and area of erosion of these formations.

In the last Kaba boring down to 211 metres, the composition is similar to the upper horizons of the borings mentioned above, *i.e.* it shows a NE direction of erosion. In the lowermost sample, taken at 216 m, the amount of brown amphibole is also larger, showing the effect of the Körös again.

This profile illustrates above all the regularity with which the alluvia of different rivers wedge out into each other. The sinking of the area is unequal, the rivers occupy each other's alluvial areas; consequently the sediments appear side by side and also above each other.

Profile N°. III *(Figure 5)* follows the line Hajdúszovát-Debrecen. The first, medium-grain sand sample suitable for examination was taken at 886 m in the Hajdúszovát N°. 1 prospecting well. According to investigations carried out in the Geological Laboratory at the Hungarian Petroleum and Gas Trust, there are Upper Pannonian beds at this depth. The heavy-mineral composition is quite different from the earlier facies discussed above. Biotite plays here the most important part. Its amount exceeds 50%. As to other minerals, brown amphibole (3,6%), magnetite (6,4%), chlorite (8,6%) and limonite (7,1%) probably altered from magnetite are also of importance. With the exception of chlorite, it is a characteristically magmatic mineral association. During the Upper Tertiary, particularly in the Helvetian stage, an intensive volcanic activity took place in this area. This activity produced also volcanic tuffites, and the Upper Pannonian sediments may partly be the result of the reworking of these products [KŐRÖSSY 1957]. Other Lower Pannonian sediments found in the Hajdúszovát well distinguish themselves by considerable amounts of chlorite and weathered minerals.

The heavy-mineral composition of the fine-grain sand sample taken in the Upper Pannonian strata of the Ebes-3 boring is very similar to that of the Lower Pannonian beds at Hajdúszovát, *i.e.* the role of chlorite is important, the weathered minerals are less considerable. In this boring, no Lower Pannonian sediments suitable for examination have been found. It is characteristic of the composition of the Upper Miocene sediments overlaid by the Lower Pannonian, that augite (2,2%), garnet (20%) and pyrite appear beside chlorite,

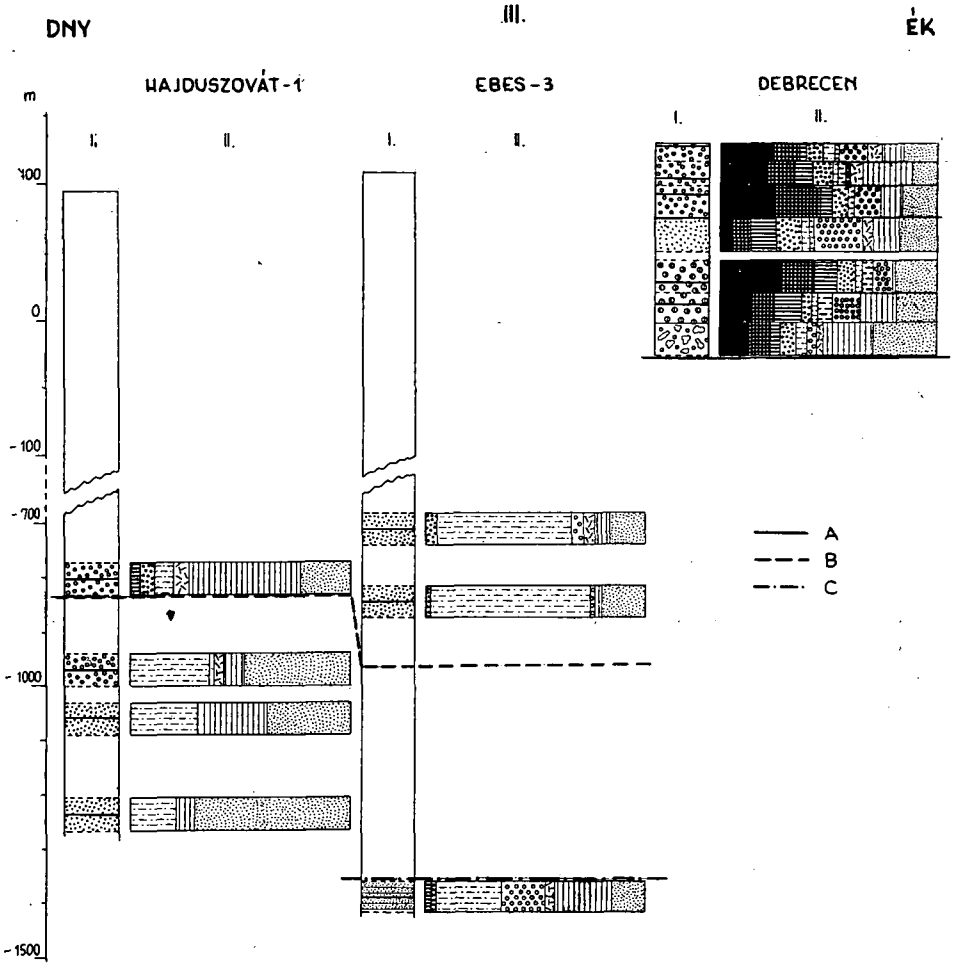

Figure 5 (Profile III). (For legends to granulometric and heavy-mineral composition see Figure 2)
A.: Lower limit of the sediments of the Tisza catchment area (?)
B.: Lower/Upper Pannonian limit
C.: Upper Miocene/Lower Pannonian limit

and that pyrite is gaining in importance. The large amount of pyrite represents a poorly aerated sea, *i.e.* a reducing environment.

In the Debrecen boring, samples from the upper horizon have been examined. With the exception of a sample from fine-grain sand, taken at 50 m, the charasteristic features in the composition of the NE rivers can be readily observed; hypersthene (12 to 28%) and augite (9 to 21%) play a particularly important role.

Figure 6 shows heavy-minerals in materials sampled at 1,3 m depth in the Debrecen boring, among other there are hypersthene, augite, garnet, mag-

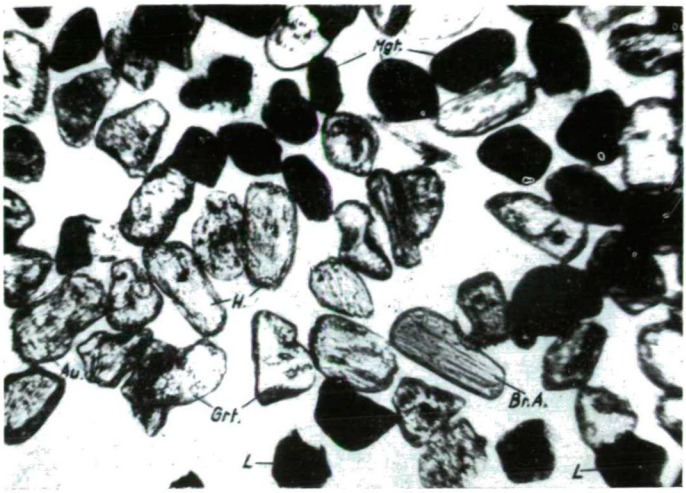

Figure 6 Heavy minerals from the 0,1 to 0,125 mm ∅ fraction at 1,3 m, in the Debrecen boring. (For embedding and magnification see Figure 3)

netite and limonite. *Figure 7* shows minerals of a sample taken at 33,5 m in the same boring, namely rounded hypersthenes as well as garnets, magnetites and limonites. Rounding-off is an effect of the wind: these grains come from the quick-sand sediments of the Nyirség, N and NW of the area.

Examinations carried out on the boring of Mezőtúr, have pointed out that also in this case the sediments were carried in, from the E and NE

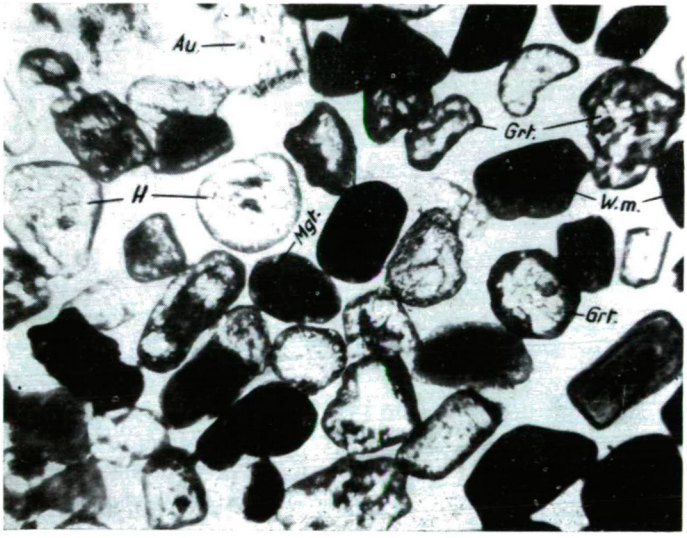

Figure 7 Heavy minerals from the 0,1 to 0,2 mm ∅ fraction, at 33,5 m, in the Debrecen boring. (For embedding and magnification; see Figure 3)

(*Figure 8* and Table). Down to 219 m, the dominant direction of transport is East, *i.e.* there are alluvias of the Körös. At 51 m, however, some NE effect can also be demonstrated: besides hypersthene and augite, brown amphiboles represent only 4,3%. Below 211 m, down to 622 m, the sediment rich in magnetite, limonite, garnet and weathered minerals. This formation may be correlated to sediments of similar composition at Pély, Kisköre, Szolnok and Gyoma, where eroded material was carried from the NW and N [MOLNÁR. 1964].

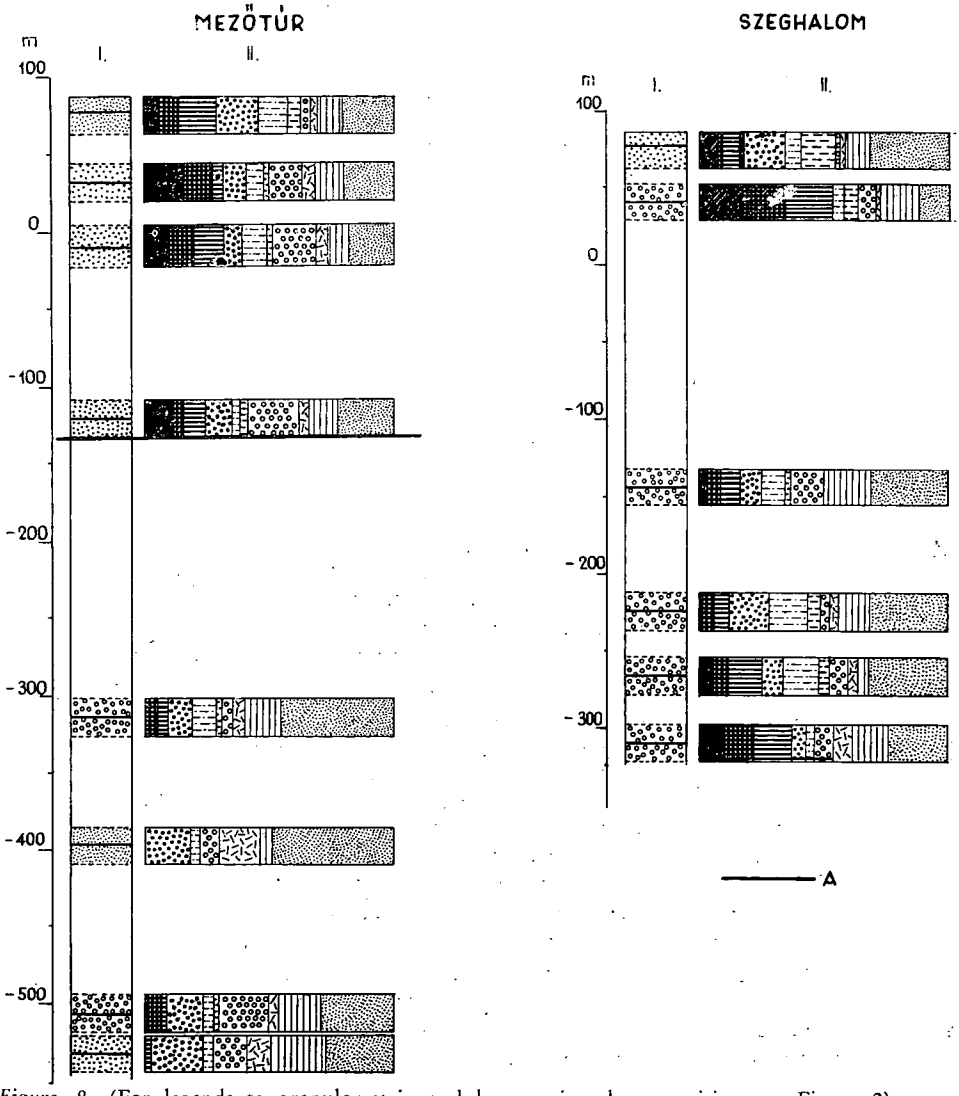

Figure 8 (For legends to granulometric and heavy-mineral composition see Figure 2)
A.: Lower limit of the sediments of the Tisza catchment-area.

With the exception of minor differences, alluvia of the Körös rivers can be demonstrated in the Szeghalom boring, down to 398 m (*Figure 8* and Table). *Figure 9* shows heavy minerals sampled at 43 m in the Szeghalom boring: for the most part it is hypersthene, augite and weathered minerals.

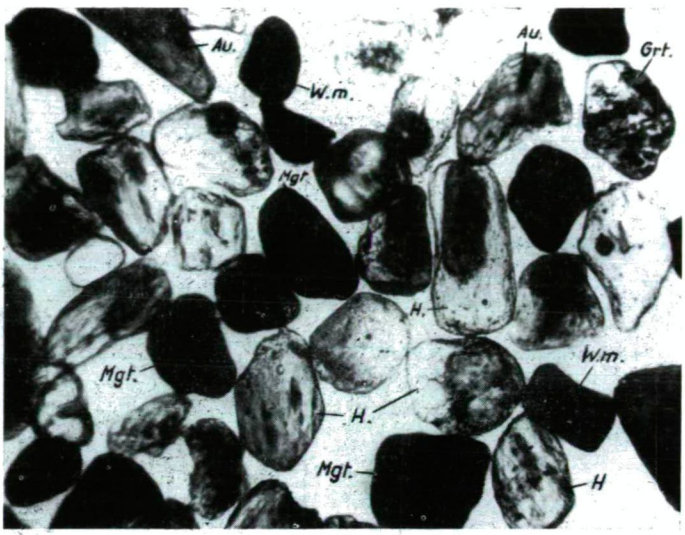

Figure 9 Heavy minerals from the 0,1 to 0,125 mm ∅ fraction, at 43,5 m, in the Szeghalom boring. (For embedding and magnification see Figure 3)

In *Figure 1*, the principal directions of stream erosion in the central part of the Tiszántúl have been outlined — and marked with arrows — on the basis of the above investigations and earlier studies. However, they do not accurately represent the alluvial area of each river, because, as it has been pointed out, the erosional areas of rivers intersect and wedge out into each other, as a consequence of uneven sinking which attracting one river or the other. In the NW, below the sediments of the present Tisza-system (the river Tisza and its affluents), an older phase of erosion can be still distinguished. It runs to the SE as far as the present Körös, and represents probably an erosion due to the Palaeo-Zagyva or Hernád-Sajó (*Figure 1*, N°. 2). The latter is overlaid by sediments showing a heavy-mineral composition similar to the alluvia of the present Zagyva, which may be traced to the East not farther than the Szolnok area, *i.e.* the deposits to be found at Törökszentmiklós have come from the NE and E (*Figure 1*, N° 3).

It is the task of further investigations to determine the directions of stream erosion of the sediments laying under the deposits of the NW and E parts of the Tisza-system (*Figure 1*, N° 3.)

According to the findings of heavy-mineral examination, the following major provinces, horizons, directions of stream-erosion and areas are to be distinguished in the Hungarian Basin:

1. Western, predominantly alpine (mainly metamorphic) stream-erosion area: the characteristic minerals of the sediments are diopside, large-size garnet,

bluish-green amphibole (hornblende), calcite-dolomite, and a small amount of metamorphic minerals (chlorite, tourmaline, epidote, zoisite, tremolite-actinolite, staurolite, kyanite). Hypersthene and augite play quite a negligible role here. These sediments were deposited by the Danube during the Lower Pleistocene (Levantian) on the western part of the Great Plain (between the Danube and the Tisza), or they were blown out from the inundation area of the Danube and were accumulated as quicksand by the prevailing wind during the Upper Pleistocene on the ridges of the western part of the Great Plain [MIHÁLTZ 1961].

2. Sediments of the Tisza area (the Tisza and its affluents) where — because of the inner Carpathian volcanoes — the distinctive and characteristic minerals are hypersthene, augite and brown amphibole. These sediments were deposited during the Pleistocene by the Tisza and its affluents over the whole territory of Tiszántúl and the northeastern part of the area laying between the Danube and the Tisza. Within this province, the following sub-provinces can be distinguished:

a) sediments coming from the alluvia of the Zagyva: besides the above-mentioned minerals magnetite and garnet are also of importance;

b) products of erosion coming from the N and NE, characterized by hypersthene and augite. These sediments were chiefly deposited by the Tisza and its affluents an the northern part of the Tiszántúl, during the Plestocene;

c) erosional product of the Körös and Maros rivers, characterized by hypersthene, augite and brown amphibole appearing together. These sediments were mainly deposited by both rivers on the southern part of Tiszántúl, during the Pleistocene.

On the basis of data available, a thickness-map of sediments belonging to the Tisza catchment area may be drawn for a quite considerable part of the Tiszántúl. *Sc.* already elaborated borings passed for the most thinnest occur-this sedimentary complex (Figure 10). The map shows that the thinnest occurrence of this formation (not more than 50 m) appears in around Macs, on the uprising Pannonian table of Hajdúság. From hereon thickening appears towards the Tisza valley and Debrecen. At Kemecse the thickness is as much as 170 m. In the western part of Tiszántúl, the formation is first thickening parallel to the Tisza, to the E of the river, up to 150 or 250 m. In the environs of Gyoma, it is thinner again, but to the East of the latter region, in the Körös area it quickly becomes quite thick. In the frontier zone the thickness of this formation is as much as 500 m. Our thickness-map reflects the events and intensity of Quaternary crustal movements. The results are in good accordance with the development of crustal movements pointed out by other methods [KERTAI 1957, BARTHA 1962].

3. Fluviatile deposits overlaid by Tisza-catchment-area sediments in the southern part of Tiszántúl: these formations are characterized by the absence (or insignificant role) of hypersthene, and small amounts of augite and brown amphibole. Among metamorphic minerals, garnet, chlorite and bluish-green amphibole (hornblende) are more or less important. A considerable part of the sediments belonging to this area comes from the inner Carpathian volcanic territory and also from the denudation or reworking of other rocks. The composition is different from the alluvia of present rivers, as they were transported by one or other of the precursors of these rivers to the South-Tiszántúl

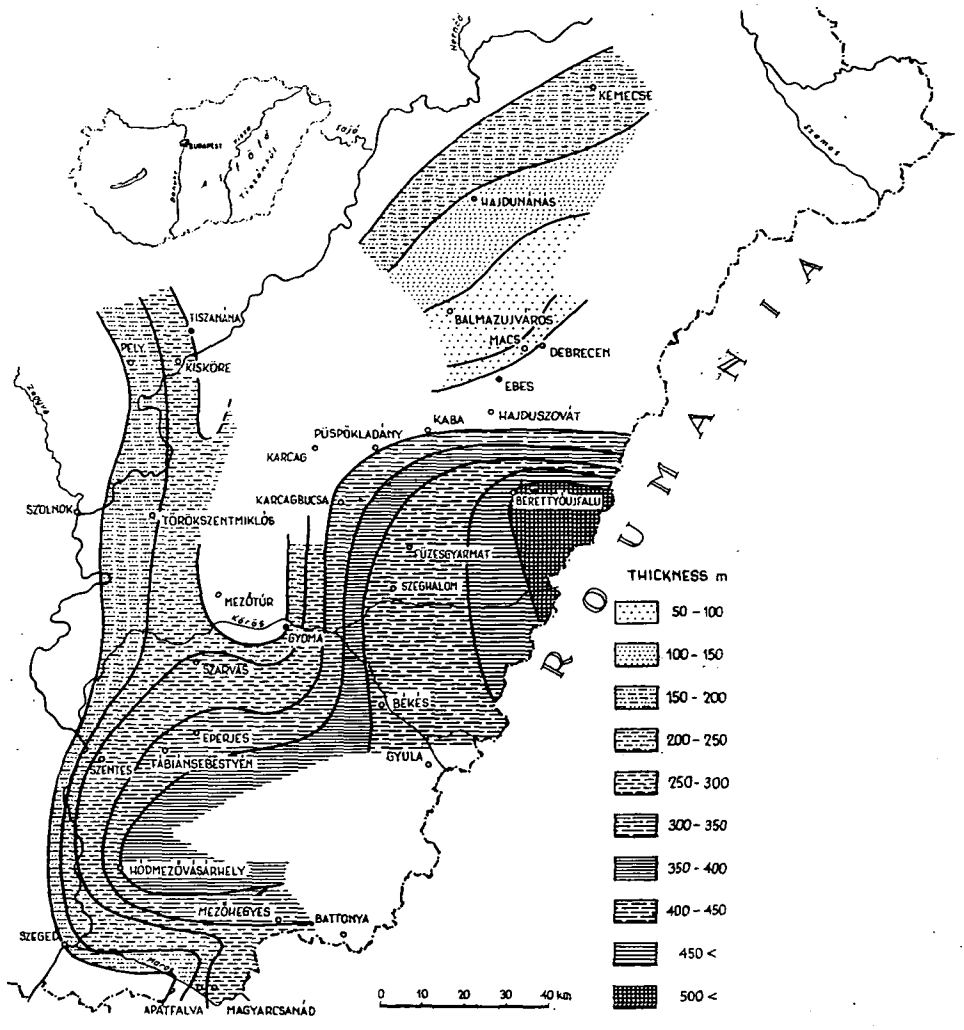

Figure 10 Thickness map of the sediments of the Tisza catchment-area.

area. With the help of the available data, it is very difficult to determine their age; they must have been deposited in the Lower Pleistocene or somewhat earlier.

4. The deposits of an assumed Palaeo-Zagyva—Sajó—Hernád river overlaid by the present-day Zagyva alluvia: this formation is characterized by larger amounts of magnetite and garnet than those found the present Zagyva-alluvia. This sediment must have been deposited during the Upper Pliocene (Levantian) and Lower Pleistocene.

5. In the northern part of Tiszántúl, the upper part of the Pannonian marine deposits are overlaid by sediments of the Tisza catchment-area; at Kemecse and Macs, these deposits are of different composition, but metamorphic minerals are dominant in their mineral association.

6. Upper Pannonian sediments, very rich in amphiboles and biotite, of North-Tiszántúl, opened by the borings of Macs, Kemecse and Hajdúszovát. This complex proves an Upper Tertiary volcanic activity in the area.

7. Lower and Upper Pannonian sediments of the southern part of the Great Plain; chlorites, the dominant minerals prove the Pannonian age of these formations.

REFERENCES

BARTHA, F. [1962]: Évaluation des mollusques des forages de recherche hydrologique dans les environs de Makó et Gyula. — Rapport Annuel de l'intitut Geologique de Hongrie sur l'année 1959. 271—296.

BULLA, B. [1962]: Physiogeographie von Ungarn. — Tankönyvkiadó, Budapest. 1—423.

CSIKY, G. [1963]: A Duna—Tisza köze mélyszerkezeti és ősföldrajzi viszonyai a szénhidrogénkutatások tükrében. — Földrajzi Közlemények *11.* 19—35.

ERDÉLYI, M. [1960]: Hydrogeologie der Hajdúság. — Offizielles Organ der Ungarischen Hydrologischen Gesellschaft *Band 40.*

JASKÓ, S. [1947]: Erosion and sedimentation in the Hungarian Basins during the kainozoic era. — Bulletin of the Hungarian Geological Society *T. 77.* 26—38.

KERTAI, GY. [1957]: The structure of the Hungarian Basins and their oil reservoirs as revealed by the results of oil exploration. — Bulletin of the Hungarian Geological Society *Band 87.* 383—394.

KŐRÖSSY, L. [1956]: Geological results of the petroleum prospecting activities on the northern part of Tiszántúl. — Bulletin of the Hungarian Geological Society *Band 86.* 390—402.

KŐRÖSSY, L. [1957]: Tiefgeologische und paleontologische Verhältnisse in Ostungarn von Gesichtspunkten der Aussichten für Erdölforschung gesehen. — Ungarische Bergbau Zeitschrift *Band 90.* 491—503.

KŐRÖSSY, L. [1963]: Comparison between the geological structure of the basin regions of Hungary. — Bulletin of the Hungarian Geological Society *Band 93.* 153—172.

KRETZOI, M. [1953]: A negyedkor taglalása gerinces fauna alapján. — Alföldi Kongresszus. Akadémiai Kiadó Bp. 89—98.

KRIVÁN, P.—NAGY, L. [1963]: Palynological method of the Upper Pleistocen profile of Tószeg—Kiskőrös region between the Danube and the Tisza. — Bulletin of the Hungarian Geological Society *Band 93.* 82—96.

MIHÁLTZ, I. [1961]: Les sediments éoliques de la Grande Plaine Hongroise. — Congres INQUA, Absractes des Travaux, Varsovie 161.

MOLNÁR, B. [1961]: Die Verbreitung der äolischen Bildungen an der Oberfläche und untertags im Zwischenstromland von Donau und Theiss. — Bulletin of the Hungarian Geological Society *T. 93.* 300—315.

MOLNÁR, B. [1962]: Sedimentpetrographische Untersuchung in Pliozänen und Pleistozänen Ablagerungen in süden des Ungarischen Tieflandes. — Acta Univ. Szegediensis Acta Miner. Petr. *15.* 43—51.

MOLNÁR, B. [1964]: On the relationship between the lithology of the abrasion area and the transported sediments. — Acta Univ. Szegediensis, Acta Miner.-Petr. *16.* 69—88.

MOLNÁR, B. [1964]: Sedimentgeologische Untersuchungen in Pliozänen und Pleistozänen Ablagerungen im Osten des Ungarischen Tieflandes. — Geologische Rundschau *Band 53/2.* 848—866.

MOLNÁR, B. [1965]: Beiträge zur Gliederung und Entstehung der jungtertiären und quartären Schichten des Donau—Theiss-Zwischenstromlandes auf Grund der Schwermineralienzusammensetzung. — Zeitschrift der Ungarischen Geologischen Gesellschaft *Band 95.* 217—225.

MOLNÁR, B. [1965]: Paleohydrographische Untersuchungen im Süd-Osten des Ungarischen Tieflandes. — Offizielles Organ der Ungarischen Hydrologischen Gesellschaft. (Manuscript).

MOLNÁR, B. [1965]: Veränderungen im Abtragungsgebiet auf der Süd-Ost Ungarischen Tiefebene im jungen Terziär und Pleistozän. — Offizielles Organ der Ungarischen Hydrologischen Gesellschaft. (Manuscript).

RÓNAI, A. [1964]: L'importance des recherches geologiques dans les regions plaines. — Rapp. Ann. de l'Institut Geol. de Hongrie sur l'Année 1961/II. Bp.

SOMOGYI, S. [1961]: Entwicklungsgeschichtliche Skizze des Wassernetzes von Ungarn. — Geographische Mitteilungen *IX. Band* Bp.

SÜMEGHY, J. [1944]: A Tiszántúl (Die Gegend links der Theiss) — Magyar tájak földtani leírása Bp. 1—20.

SÜMEGHY, J. [1955] A magyarországi pliocén és pleisztocén. — Akadémiai doktori disszertáció (Manuscript).

SZEPESHÁZY, K. [1962]: Contribution to the subsurface geology of the Nagykőrös—Kecskemét area. — Bulletin of the Hungarian Geological Society *Band 92.* 40—52.

SZÉLES, M. [1965]: Oberpliozäne bunte Tone in den Erkundungsbohrungen aus Kohlenwasserstoffe in der Grossen Ungarischen Tiefebene. — Zeitschrift der Ungarischen Geologischen Gesellschaft *Band 95.* 226—229.

URBANCSEK, J. [1960]: Hydrogeologische Schlüsse aus der spezifischen Ergiebigkeit der artesischen Brunnen in der ungarischen Tiefebene. — Offizielles Organ der Ungarischen Hydrologischen Gesellschaft *Band 40.* 398—403.

URBANCSEK, J. [1962]: Szolnok megye vízföldtana és vízellátása. — A Szolnok Megyei Tanács Végrehajtó Bizottságának kiadása. Szolnok.

DATA ON THE GEOLOGICAL AND MINERALOGICAL KNOWLEDGE OF LOWER LADINIAN SCHISTS IN THE BÜKK MOUNTAIN

by

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In the course of the industrial prospecting for raw materials, carried out on the west margin of the Bükk Mountain [TAKÁTS, 1964], the schist area situated on the north side of the limestone range of the Bélkő has been investigated in detail *(Fig. 1)*. By the investigations good basic and comparative data to the mineralogical knowledge of the Lower Ladinian schist formation in the Bükk Mountain has been obtained.

GEOLOGICAL CONDITIONS

Geological structure. We explored the schist formation in detail on the Vanna field of Bélapátfalva. This area is situated on the west border of the mesozoic basement of the Bükk Mountain. Among the published geological works of other authors on the area and its close surroundings, the studies of Z. SCHRÉTER [1943, 1954a, 1954b, 1960], S. JASKÓ [1953] and K. BALOGH [1964] are the most important ones.

During the years 1963, on the prospecting area of the Vanna field, Bélapátfalva, thirty-seven 1—3 m deep exploring shafts, one 12 m deep, two 30 m deep and eight 50 m deep core drillings of 76 mm ∅ were made.

The selecting of the places for exploratory drillings was strongly influenced by the transporting difficulties inherent to the ground, but in spite of that we sought to place them in such manner that they should 1. form, as far as possible, a regular network, 2. clear up the connections between the geological and morphological conditions [TAKÁTS—VITÁLIS, 1965].

The prospecting area of the Vanna field is built up dominantly by the schist formation of the Lower Ladinian. The schist formation is not of homogeneous origin, it contains interposed beds of limestone and sandstone, subordinately calcareous schist and flint-shale of varying thickness.

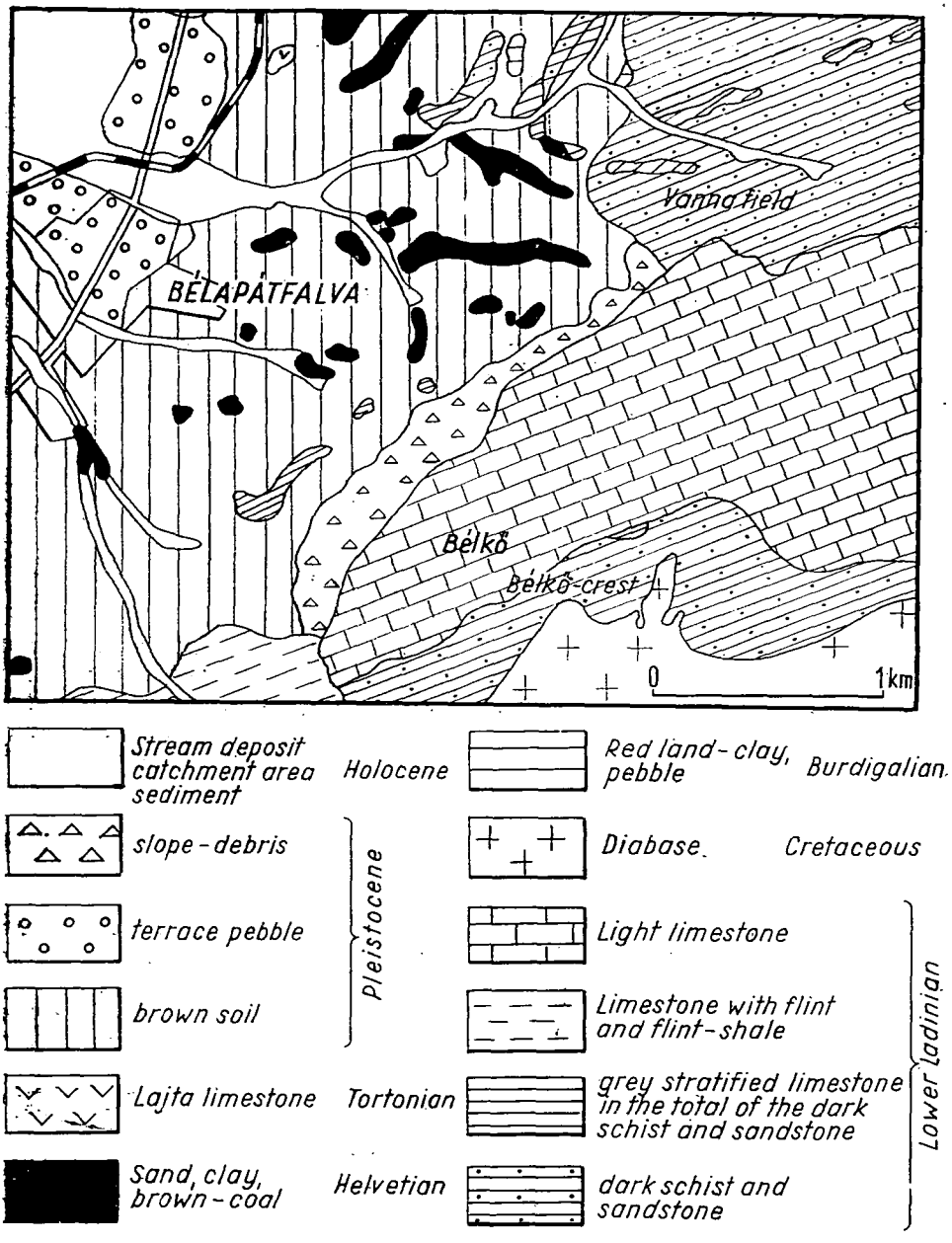
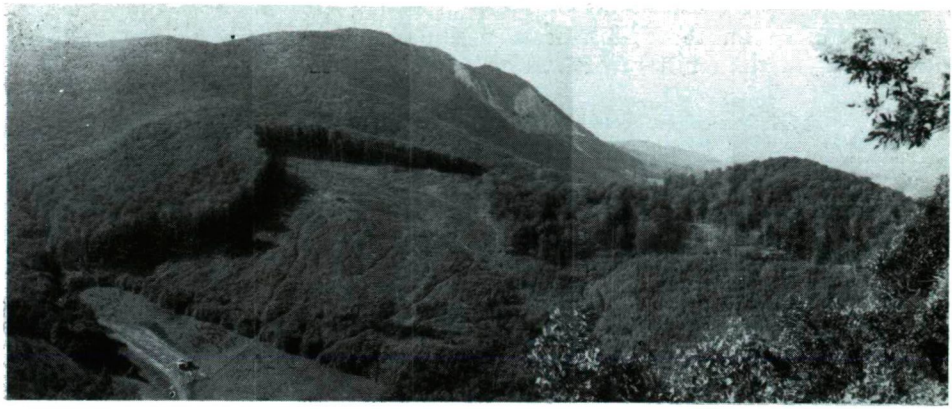


Fig. 1. Sketchy geological map of the surroundings of Bélapátfalva (after SCHRÉTER, Z.)

The schist formation less resistant against erosion, nestling to the sides of the steep NW—SW limestone range of the Bélkő is conspicuous even from the inclines sloping in a milder extent. *(Picture 1).* On the other hand, the peaks, ridges or crests morphologically slightly emerging out from the schist



Picture 1. The perspectivic picture of the prospecting area of the Vanna field Bélapátfalva. (Above the midline of the picture the limestone quarry of the Bélkő, on the right of the picture the peak of Őzlövő.)

formation attract the attention upon the limestone and sandstone formations settled into the schist complex (e. g. Őzlövő peak).

Upon the schist, sandstone, and limestone formations of Lower Ladinian, a Pleistocene cover of 0—5 m thick schist (subordinately limestone and sandstone) rubbled brown and red-brown clay is settled.

The extent and thickness conditions of the geological formations building up the area of prospecting are illustrated on the engineer-geological map [Takáts and Vitális, 1965; Vitális, 1965] as well as on the sketchy geological profiles displayed in *Figure 2*.

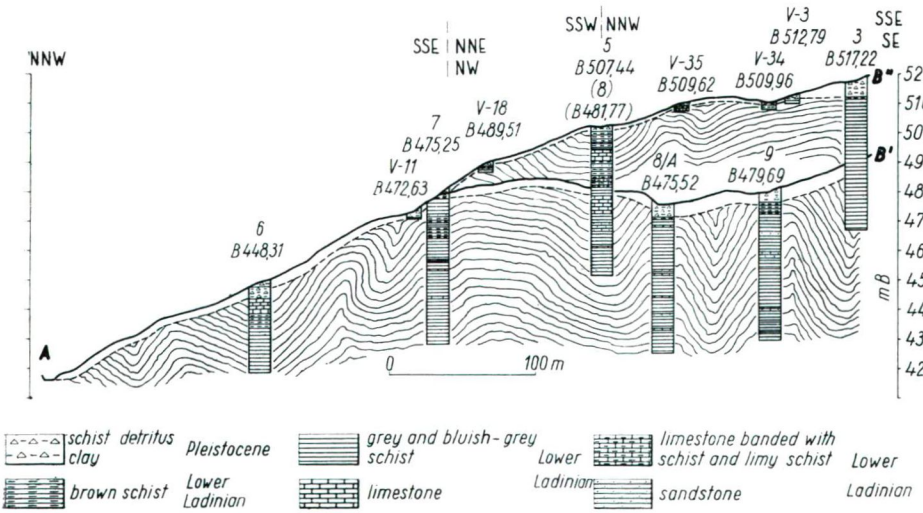


Fig. 2. Sketchy geological profile of the Vanna field.

The geological conditions of the prospecting area at the Vanna field are displayed even on the SM (silicate module) maps illustrating the industrial utilisability of the schist raw materials *(Figures 3—5)*.

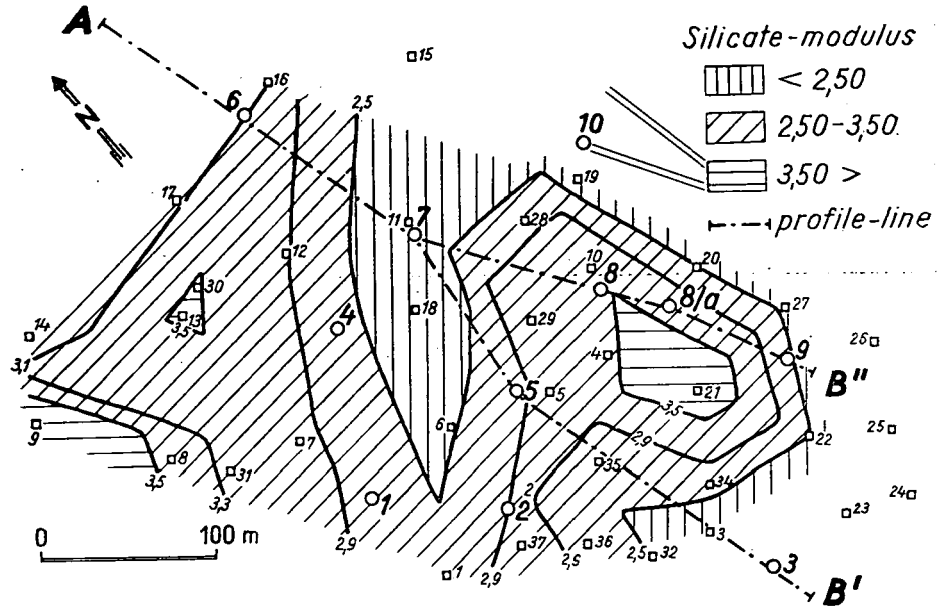


Fig. 3. The SM map of the Pleistocene clay covering of the prospecting area of the Vanna field.

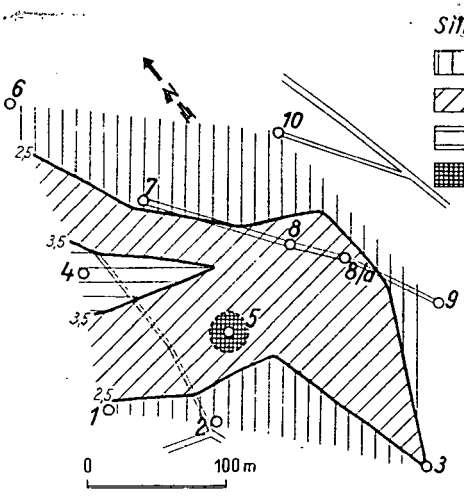


Fig. 4. The SM map of the Lower Ladinian schist layers of the prospecting area of the Vanna field at 20 m below the surface.

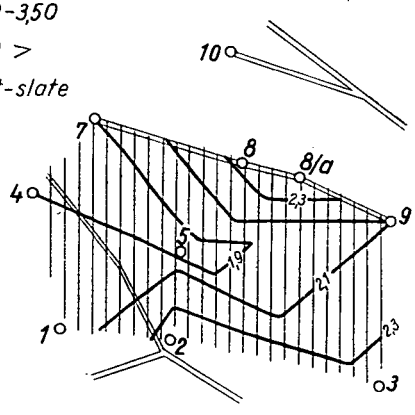


Fig. 5. The SM map of the Lower Ladinian schist layers of the prospecting area of the Vanna field at 40 and 50 m below the surface.

The SM maps were constructed with interpolation on the basis of the SM values concerning the corresponding depths. We chose the numerical values of the contour lines connecting the places of same quality, respectively separating the parts of different quality on the basis of the frequency of values gained from the results of examinations. We drew the line on the basis of frequency as well for the summarizing cartographical delineation respectively separation of the SM values at 2,50, between 2,50 and 3,50 and above 3,50.

For the multiple control of the stratification we had electric log examinations too, made in two borings. On the basis of the carottage profiles made in the 8/A and 9 borings, the boundaries of the layers can be marked out reliably, at the determination of the material, on the other hand, they depended mostly on those given by the boring. According to the resistance profiles the quality of the schist varies even within an appointed layer *(Figure 6)*. The

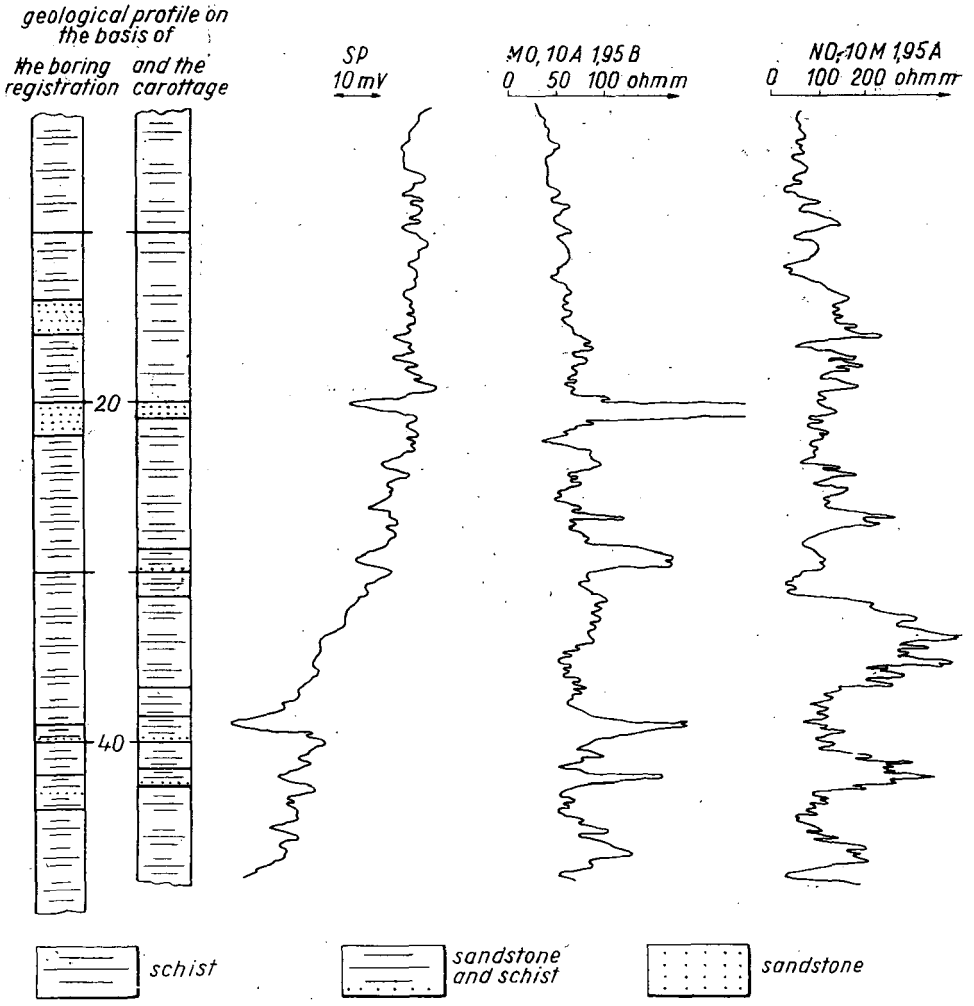


Fig. 6. Electric well log of the boring N° 9.

boundaries of layer marked out in the schist formation display the rough differences of quality.

Mountain structure. For the prospecting area of Vanna field the folded forms are characteristical. The strike of the several geological formations is in agreement with the roughly NE—SW strike of the Bélkő range. The folded forms of the schist complex could be well studied, peculiarly in the exploring shafts, in which we observed very strong dips of the strata with diverse, respectively caotic foldings. The dips measured had mostly SSE and NW courses, the minimal angle of dipping was 32°, the maximal 84°.

Based upon these it could be supposed, of course, that the schist complex penetrated with borings was also folded. Therefore, on the rudimental profile made of the area *(Figure 2),* the strata of identical petrographic development penetrated by the several borings, could not be connected with absolute certainty, we demonstrated only the strong folding of the complex.

Hydrogeological conditions. No water appeared during the prospecting borings in the Lower Ladinian formation. The schist complex can be considered watertight. The smaller limestone lenses wedged into the schist are permeable to water, but they are practically dry as they can obtain only a very poor water supply through the schist.

The whole prospecting area of the Vanna field is situated above the karstwater surface known in the surroundings (approximately 365 m above sea level). The bottom B of the boring No 6 deepened to the least sea level height, reached 418,31 m, thus the opening of a mine in the area is, with respect to the karstwater, not dangerous.

TEST RESULTS

In the course of examination of the possibilities for utilizing the Lower Ladinian schist for industrial purposes, — for characterizing the raw material — the chemical and mineralogical composition, the burnability, the nodule strength as well as the grindability of the samples was determined.

The determination of the mineralogical composition — with consideration of the chemical composition — took place by the reconciliation and evaluation of the results of different instrumental examinations. The procedures applied were: dilatometry, X-ray diffraction, differential thermal analysis and derivatographic examinations.

Dilatometers of BOLLENRATH-type, made by LEITZ, were used. The heating rate was 7 C°/min. in every case, the highest temperature attained was 1000°C. Samples were prepared by pressing, adding tylose if necessary.

X-ray diffraction examination was done partly by DEBYE-SCHERRER procedure (with MIKROMETA apparatus), partly by diffractometer procedure (with RIGAKU-DENKI apparatus). In all cases Cu Kα radiation was applied with nickel filter.

The differential thermal analysis (DTA) records served the quick information. These were made with the „rapid" DTA apparatus of KLIBURSZKY—FÖLDVÁRI. To the quantitative evaluation DTA, TG and DTG graphs were made with the derivatograph of PAULIK—PAULIK—ERDEY. The highest temperature attained was in every case 1000°C, recording time was 90 minutes.

Table I. Total chemical analysis

Place and depth of sample taking (m)	Name of rock	Loss on ign.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	S M
		weight %								
6. boring										
10—14	brown schist	5,39	55,50	22,63	9,10	0,86	0,42	0,95	3,34	1,75
20—24	bluish grey schist	4,60	58,21	21,06	8,70	0,50	0,18	0,93	3,43	1,96
28—30	bluish grey schist	5,87	53,16	23,79	8,25	1,18	trace	0,91	3,16	1,66
7. boring										
19—21,5	bluish grey schist	4,55	60,64	18,95	7,60	0,50	0,11	1,02	2,50	2,28
40—44	grey schist	4,89	56,78	22,63	7,50	1,10	3,08	1,08	3,24	1,88
9. boring										
16—20	grey schist	5,72	57,57	18,47	9,82	1,28	0,18	1,35	2,30	2,03
39,7—42	grey schist	5,51	55,40	22,26	8,12	0,60	0,22	1,05	3,19	1,82
10. boring										
20—21	bluish grey schist	5,26	57,59	20,56	8,40	0,49	0,72	0,87	3,00	1,99
27—30	bluish grey schist	5,68	58,72	19.05	8.59	0,69	0,29	0,76	2,57	2,12

* In the value the Al_2O_3 component, the TiO_2 and the MnO take as well.

Chemical investigations. Not all samples were examined, only types characteristic for the occurrence. Total analyses were made of nine samples *(Table 1).* From one hundred and ten samples the most important characteristics were determined only; the percentage of silica, aluminum and iron oxide as well as, in some cases calcium oxide.

As the matter in question is a raw material of the cement industry, in the judging of the material the ration of silicic acid to the R_2O_3 is playing a significant part. Therefore, for the simplified characterizing, the value of the silicate modulus (SM) was computed. On the basis of the complete and partial chemical analyses the SM value of the clay and schist is ranging in the bulk between 1,66 and 3,44. As it is demonstrated in the SM maps *(Figures 3—5)* as well, the SM value is reduced in the deeper levels.

The CaO value is raised in some cases by calcareous interbeddings. Potassium is always present in greater amount than sodium.

DTG and DTA examinations. Diagrams published in *Figures 7—12* show that the DTG curves of all samples examined are of illitic character, as they show a strong endothermic peak between 500 and 600°C. The presence of quartz increases the height of this endothermic peak, but an extra quartz peak appears only if the quartz is present in a dominant quantity *(Figure 11).*

Some curves *(Figure 8)* indicate strongly the calcite content. On most curves a decided bulging can be observed about 450 °C, before the endothermic peak of 550 °C, indicating the crystal-water loss of illite. This hints to the presence of some pyrite content.

Thermogravimetrical (TG) curves show that all samples — with the exception of calcareous samples — lose their bound water between 500 and 600°C. This means illite and kaolinite respectively. The carbonate-containing

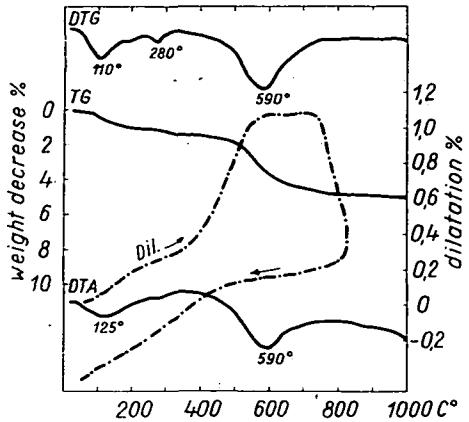


Fig. 7. The thermic curves of the Lower Ladinian schist from the shaft No V—25, at 2,2 m depth.

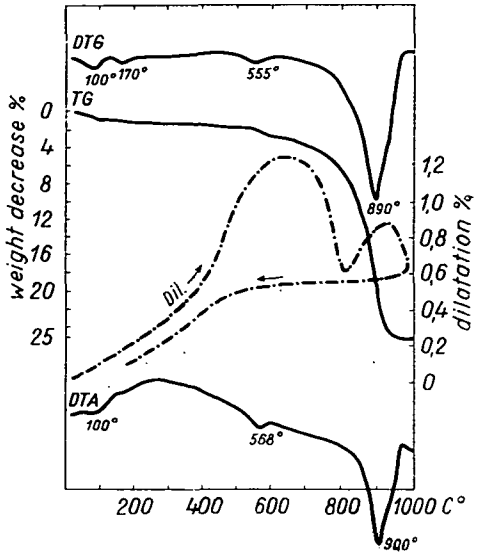


Fig. 8. The curves of limy Lower Ladinian schist from the shaft No V—37, at 2,0 m depth.

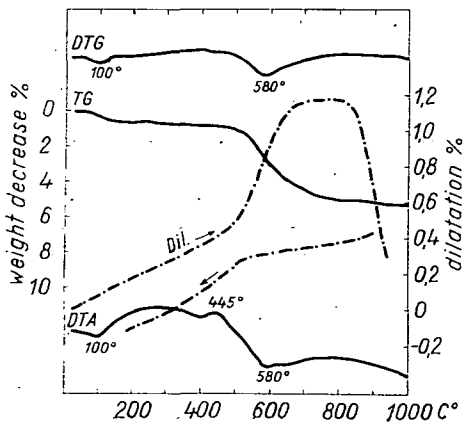


Fig. 9. The thermic curves of the bluish grey Lower Ladinian schist derived from the boring No 6, at 20—21 m depth.

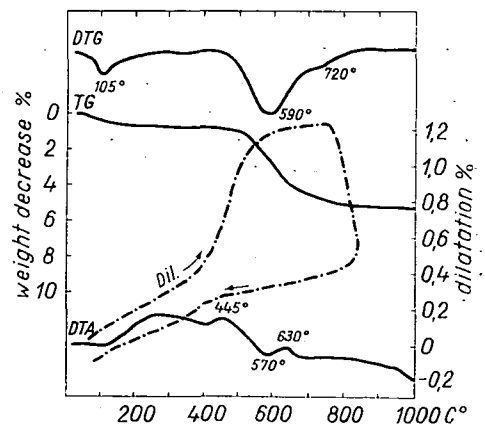


Fig. 10. The thermic curves of the bluish grey Lower Ladinian schist from the boring No 6, at 29,30 m depth.

samples showed above 800°C a strong weight loss, as indicated by the intense decline of the TG curves. The peak of the derived TG curves (DTG curves) are much the same as those of the DTA curves and indicate the initial and terminating temperature of the reactions. On the DTG curves of a few samples the minima indicating the loss of weight can be recognized even about 300°C

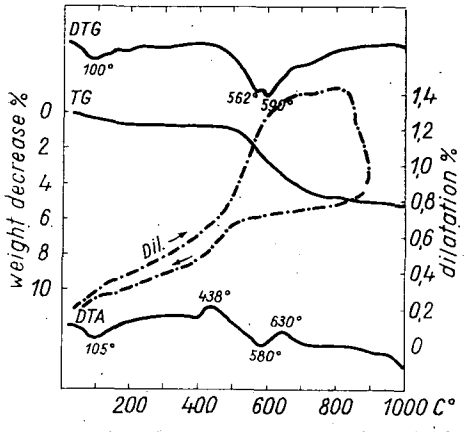


Fig. 11. The thermic curves of the bluish grey Lower Ladinian schist from boring No 7, at 19—20 m depth.

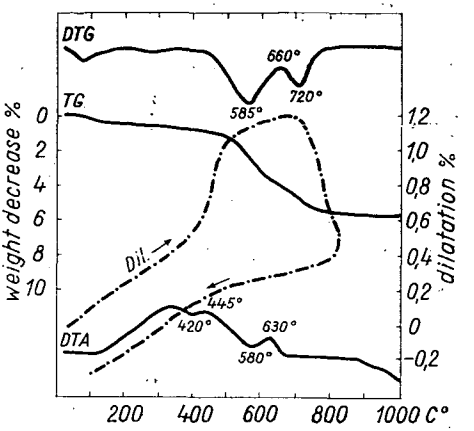


Fig. 12. The thermic curves of the grey Lower Ladinian schist derived from the boring No 9, at 19—20 m depth.

(this is indicated by a quite slight inclination of the TG curves too), which means that the samples contain hydrargillite as well.

Dilatometric examinations. The results are illustrated in *Figures 7—12* as well. The dilatation curves are very similar. The most typical is the curve of *Figure 9.* The initially moderate dilatation is followed, after 500°C, by a more intensive dilatation up to 600°C. At this temperature the steepness of the curve decreases, and after a horizontal phase lasting up to 800°C, the curve indicates a rapid shrinkage. This is the typical illite curve. The ascending phase of the curve is changing from sample to sample; this change can be brought about by kaolinite and quartz content. Cooling curves were prepared as well, to get some information about the quartz content of the material. As it can be seen in the figures, the cooling curves indicate in every case a quartz content, in some samples even in a considerable quantity. In *Figure 8* the characteristic calcite curve can be seen. The sample shows above 700°C an intense shrinkage, but above 800°C it is swelling again to begin the final shrinkage after 900°C.

The samples, the dilatograms of which show on the ascending branch above 200°C a smaller or greater break, as the sample illustrated in *Figures 7—10* and *12,* contain besides quartz a great quantity of kaolinite. The characteristic dilatogram of the kaolinite can not develop on account of the great quartz and illite content.

X-ray examinations. In accordance with dilatometric examinations quartz appears in all samples in dominating quantity. The kaolinite and illite can be recognized with definite reflections. In most samples feldspar can be observed too by its most intensive reflection. In some samples montmorillonite can be demonstrated too, though its quantity is on the basis of the intensity dates only slight. In the calcareous schist samples calcite lines appear as well.

It is interesting that there are a few samples in which illite reflections could not be observed. These contained much quartz and kaolinite. The intensity values of the kaolinite are rather low, which means that the degree of crystallization is low.

Mineral composition. On the basis of analytical data and instrumental examination it can be stated that the mineral composition of the samples is diversified. In all samples great quantities of quartz can be found, not only in the sandstone but in the schist samples as well. This statement can be derived chiefly from dilatometric and X-ray examinations. The clay minerals are represented by illite and kaolinite. Their absolute quantity and their quantity in relation to each other differs from sample to sample. In some of the samples no illite reflections were observed, in other samples kaolin was absent. The dilatometric and derivatographic curves indicate a greater illite than kaolinite content. The considerably greater potassium than sodium content is a hint to illite content as well. On the DTA curves the exothermal peak of the kaolinite is absent, but this may happen and suggests the conclusion that the degree of crystallization in the kaolinite is rather poor.

In some samples montmorillonite was found by X-ray, but the intensity of the reflections is small, thus its quantity is not considerable. This explains that the clay is not plastic and its nodule strength value is also slight.

Feldspar was also detected in many samples, though mostly by a single reflection only, thus its quantity might be minimal. DTA curves indicate pyrite in most of the samples. As by X-ray it was not demonstrable, its quantity might be max. 1—2%. By the evidence of derivatograms some samples contain hydrargillite in a smaller quantity.

The carbonated samples contain a considerable amount of calcite.

Examinations of burnability, nodule strength and grindability. Burnability examinations were carried out with raw meals of 0,9 saturation. To the raw flours we used so called „limestone of Berva" from Felnémet. The burning took place at 1400°C for 30 minutes. As it is known, the free CaO content indicates the burnability. The burnability was very variable, which is — considering the analytical data — considerable, for both the SM value and the AM value influence the burnability to a considerable extent. Accordingly the schist of average composition — in accordance with the literature data [DOLEZSAL, 1961] — has low burnability.

The nodule strength examinations were carried out on raw meals of 0,9 saturation, made of limestone of Felnémet, their grinding fineness being $R_{0,09}=10\%$. From each sample four tests were moulded with different humidity and heat-treated with GUY's method, and the setting stability measured. According to the data of the examination the granulability is rather poor, which can be explained by the scarcity or total absence of montmorillonite.

The data of *the grindability examinations* answered the expectations. This examination was carried out of course only with the sandstone and limestone samples.

REFERENCES

BALOGH, K. [1964]: A Bükkhegység földtani képződményei. — Die geologischen Bildungen des Bükk-Gebirges. — Földtani Intézet Évkönyve *XLVIII.* 241—720. Budapest.

DOLEZSAI, K. [1961]: Cementgyári nyersanyagok égethetőségi vizsgálata. — ÉAKKI 172. sz. Kutatási jelentés, Budapest.

JASKÓ, S. [1953]: Bükkmogyorósd, Balaton, Szilvásvárad és Bélapátfalva környékének földtani leírása. — Description géologique des environs de Bükkmogyorsód, Balaton, Szilvásvárad et Bélapátfalva. — Földtani Intézet Évi jelentése, 1951. 11—16. Budapest.

SCHRÉTER, Z. [1943]: A Bükk-hegység geológiája. (Beszámoló a Földtani Intézet vitaüléseinek munkálatairól. — Földtani Intézet 1943. évi jelentésének függeléke. 378—411. Budapest.)

SCHRÉTER, Z. [1954]: Földtani újratérképezés Szilvásvárad környékén. — Relevé géologique dans les environs de Szilvásvárad. — Földtani Intézet Évi Jelentése, 1952. 135—142. Budapest.

SCHRÉTER, Z. [1954]: A Bükk-hegység régi tömegének földtani és vízföldtani viszonyai. — Hidrológiai Közlöny, 34. 287—294. és 369—381.

SCHRÉTER, Z. [1960]: Die geologischen Verhältnisse des Bükk-Gebirges. — Karszt- és Barlangkutatás, 1959. I. 7—36. Budapest.

TAKÁTS, T. [1964]: Kötőanyagipari nyersanyagok kutatása. — Az ÉAKKI tízéves tudományos működése, 1953—1963. 15—26. Budapest.

TAKÁTS, T.—VITÁLIS, GY. [1965]: A Bélapátfalva, Vanna réti agyagpala kutatás. ÉAKKI Tudományos Közlemények. 15. Budapest. In print.

VITÁLIS, GY. [1965]: A Bélapátfalva, Vanna réti agyagpala kutatási területi mérnökgeológiai térképe. — Építésföldtani Szemle, Budapest. In print.

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